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INDUSTRIAL AND MANUFACTURING CHEMISTRY

PART I

ORGANIC

A PRACTICAL TREATISE

BY

GEOFFREY MARTIN, D.Sc. (Lond. and Bristol), Ph.D., F.I.C., F.C.S.

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NOTE TO THE FOURTH EDITION

IN the present edition the various sections have been brought up to date. A new section has been added on the Tobacco Industry from the pen of Mr. S. E. Hodgkinson; a short description of the cracking of oils for motor spirit and benzene toluene has been added. The modern nitro-cellulose varnishes and dopes are now specially dealt with, and modern methods of bleaching linen yarns are described.

Many minor corrections and additions—too numerous to be mentioned here—have been made, thanks largely to communications from many practical men working in the trades dealt with. To these the Editor takes this opportunity of thanking them for their co-operation and help, and he trusts that they will continue to favour him with further criticisms and suggestions.

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Industrial Chemist and Chemical Patent Expert

Together with a Chapter on Recent Oxidising Agents

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Second Impression

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PREFACE

THE present volume deals with some of the most important products of the Chemical Industry. The element Chlorine has steadily increased, decade by decade, in commercial importance until the present time. The world's annual production of this element cannot be much less than 150,000 tons—enormous amounts being used in the manufacture of bleaching powder, hypochlorites, chlorates, perchlorates, and certain complex carbon compounds from which synthetic dyes are derived.

The magnitude of the bleaching industry and its close connection with the textile and dyeing trades are too well known to need further comment here.

It is well, however, to refer to a change which is gradually coming over this branch of industry. Whereas formerly practically all bleaching was performed by means of chlorine absorbed in lime—the well-known bleaching powder—at the present time a considerable and growing quantity of bleaching liquids are produced on the place of use by electrolysing brine. Special attention has been devoted to this recent development, as well as to the subject of electrolytic chlorine and alkali. The comparative neglect of electrolytic methods in Great Britain, and their highly developed condition in the United States and in Germany (where no less than 66 per cent. of the bleaching powder made is produced from electrolytic chlorine), are matters of serious consideration at the present time; indeed, further neglect may lead to the undermining of the British Alkali Industry. In the present book the most recent available information is given of electrolytic methods for manufacturing chlorates and perchlorates—substances especially valuable on account of their oxidising and explosive properties.

Bleaching powder has been dealt with at considerable length. This substance has acquired especial importance on account of its valuable disinfecting properties. Indeed, the large scale employment of bleaching powder in modern warfare has been largely responsible for the greatly lowered mortality due to disease.

The employment of chlorine gas in warfare—first practised by the Germans in 1915—has turned the attention of the whole world to liquid chlorine, and hence no apology is needed for the detailed account which is given of the methods employed for liquefying and storing this substance. Indeed the employment of poisonous gases by the Germans has brought home at last to the general public that this is essentially a chemical war, and that chemistry is destined to play a great part in the future in deciding the rise and fall of nations. Our grave neglect of chemical science in the past has undoubtedly cost the country many thousands of valuable lives and hundreds of millions of pounds.

The final chapter, written by Mr G. W. Clough, gives a concise account of some modern oxidising agents which have become important within recent years. The article deals with peroxides, persulphates, percarbonates, and similar substances; and it is hoped will afford valuable information which otherwise would have to be obtained from scattered and often inaccessible periodical literature.

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CHAPTER I

The Manufacture of Chlorine by the Weldon and Deacon Processes

CHAPTER I

THE MANUFACTURE OF CHLORINE BY THE WELDON AND DEACON PROCESSES

LITERATURE

For a full account of the subject, including literature, see G. Lunge, "Sulphuric Acid and Alkali Industry." 1915.

Geoffrey Martin and E. Dancaster give a full account of the properties of gaseous and liquid chlorine in Vol. VIII. of "Modern Inorganic Chemistry." Edited by Newton Friend. 1914.

See also Holbing, "Fortschritte in der Fabrikation der Anorganischen Sauren, der Alkalien, des Ammoniaks und Verwandter Industriezweige." Berlin, 1905.

See also the references under "Deacon Process," p. 7; under "Electrolytic Chlorine and Alkali," p. 13; and under "Liquid Chlorine," p. 29.

Until recently almost all the chlorine produced was made from hydrochloric acid, either by the Weldon or by the Deacon process, the hydrochloric acid for the purpose being obtained by treating salt with sulphuric acid (salt cake process). Within the last few years, however, more than half the world's supply of chlorine has been obtained by electrolysis of brine solutions, which latter method yields, according to slight alterations in the conditions of electrolysis, chlorine, chlorates, bleaching solutions, also caustic soda and sodium carbonate. An account of each of these methods will be given in due course.

The main use of chlorine is for the bleaching of paper and cotton. The oldest bleaching fluid put on the market was "Eau de Javel" (Paris, 1786), a solution of potassium hypochlorite. Later, this was displaced by the cheaper and more convenient solid "bleaching powder" (Tennant, 1799, in Glasgow), which at the present time is manufactured on a very large scale, and is sold under the trade names of "chloride of lime" and of "bleaching powder." More recently, after a century-long monopoly, a serious rival to bleaching powder has arisen in the electrolytically produced bleaching fluids ("electrolytic bleaching"), which are produced by electrolysis of brine on the place of use, because the liquids soon decompose on standing.

The main use of chlorine is, therefore, the production of these bleaching materials. However, large quantities of chlorine are now employed for chlorinating various organic products in the intermediate stages of synthetic dye production, the chlorine for the purpose being put on the market in a liquid form in steel cylinders.

The manufacture of chlorates of sodium and potassium has attained considerable importance, these products being used for the production of explosives and for oxidising purposes.

Statistics.—According to Bernthsen (1909) the world's production of bleaching powder is estimated at 300,000 metric tons yearly, Germany producing in 1905 some 85,000 tons, 50,000 of which were made from electrolytic chlorine. Europe at present produces some 9,000 tons of chlorates.

The following figures relating to German chemical industry are interesting as showing the great variations in price and quantities of the products, fluctuations traceable to the rise of electrolytic bleaching processes:—

Bleaching Powder:—

	1895.	1905.	1909.
Excess of export over import.	2,300 tons at 150 marks.	30,300 tons at 90 marks.	26,100 tons at 90 marks.

The German import of potassium chlorate is given by the following figures:—

	1895.	1905.	1909.
Excess of import over export.	75 tons at 820 marks.	1,020 tons at 530 marks.	100 tons at 620 marks.

The manufacture of chlorates is most advantageously carried out in countries provided with cheap water power, and the industry is rapidly developing on such sites.

The Weldon Process.—The process rests on the oxidation of hydrochloric acid by means of manganese dioxide. The exact nature of the reaction is disputed,[1] but is usually represented by the equations—

$$\underset{\substack{\text{Manganese}\\\text{dioxide.}}}{MnO_2} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{4HCl} = \underset{\substack{\text{Manganese}\\\text{tetrachloride.}}}{MnCl_4} + 2H_2O.$$

$$\underset{\substack{\text{Manganese}\\\text{tetrachloride.}}}{MnCl_4} = \underset{\substack{\text{Manganese}\\\text{dichloride.}}}{MnCl_2} + \underset{\substack{\text{Chlorine}\\\text{gas.}}}{Cl_2}.$$

The manganese dioxide (pyrolusite, black oxide of manganese), MnO_2, is largely mined in Spain and in the Caucasus mountains. It is impure, usually containing iron. Its value, technically, is judged by the amount of "available oxygen" it contains.

The available oxygen is estimated as follows:—

Manganese dioxide is dissolved in sulphuric acid in the presence of a known excess of ferrous sulphate. The amount of ferrous iron oxidised to the ferric state is then determined by volumetric titration in the ordinary way.

Another process is to heat the manganese dioxide with hydrochloric acid. Chlorine is evolved equivalent in value to the "available" oxygen. This chlorine is received in a solution of potassium iodide, and the iodine set free is then estimated by titration with sodium thiosulphate. For details of these processes books on chemical analysis should be consulted.

By a special process to be described the used manganese dioxide is recovered and used again, so that in practice the only natural manganese dioxide required is that needed to cover the unavoidable working losses, which usually amount to 3 per cent. on every 100 parts of bleaching powder made.

The working details of the process are as follows (see Fig. 1):—

A is the chlorine still. It consists of a still made out of some 6 or 8 granite or sandstone slabs fastened together. The still is usually 9 or 10 ft. high and about 6 or 7 ft. in diameter. At the top is an earthenware inlet pipe, and at the bottom is a pipe for running off the manganese chloride liquors. A steam inlet pipe, encased in earthenware or sandstone, passes nearly to the bottom of the still, and allows its contents to be heated by live steam.

The calculated amount of hydrochloric acid[2] having been run into the still, the calculated amount of manganese dioxide in the form of recovered Weldon mud is allowed to gradually flow in, and chlorine gas is developed in a regular stream. When the action slackens the contents of the still are heated by live steam until the liquid boils, when the reaction $MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$ is completed. The hydrochloric acid will be almost completely used up if it is of the right strength, viz., 18°-20° Bé.

If, instead of Weldon mud (recovered manganese dioxide), natural manganese dioxide is to be used, the pyrolusite, broken into coarse pieces, is placed in a different still from that used for Weldon mud, being placed on sandstone or earthenware grids, and steam is then blown in.

---

[1] See discussion, Geoffrey Martin and Dancaster's "The Halogens."

[2] One cannot partially replace the HCl by H_2SO_4, otherwise the Weldon recovery process becomes impossible.

As a rule, in big works several stills are in use at once, the chlorine being led into a common conducting pipe. In order to cut out any given chlorine still the following device is resorted to:—Each still has an exit tube B (Fig. 2), which communicates with the main chlorine conducting pipe A by means of a U tube shaped as in the figure, the tubes being joined up chlorine-tight through a water seal at *cc*. When it is decided to cut off the chlorine generator connected with B, all that is necessary is to pour water down *e* so as to fill up the U tube with water.

When communication between B and A is to be reopened, the water in the U tube is run off by withdrawing the stopper *f*.

Some small factories (such as bleachers) generate their own chlorine in earthenware generators, such as that illustrated in Fig. 3. More usually, however, these small users buy chlorine in the liquid state (at less than 6d. per pound) in steel cylinders (see p. 29).

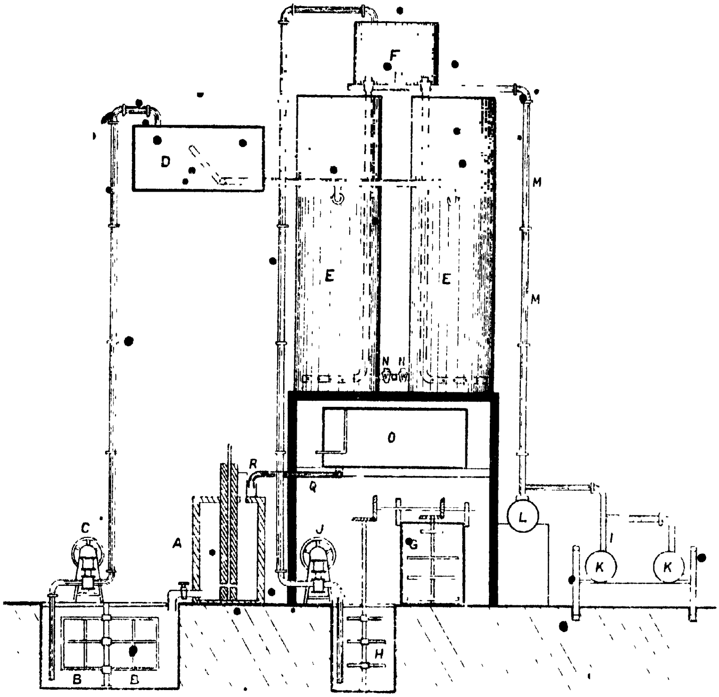

FIG. 1.—The Weldon Process of Chlorine Manufacture.

When the action is completed the acid manganese chloride liquors are run from the still A (Fig. 1) into the cemented tank B, which is provided with a mechanical stirring apparatus and a pump C. Here the liquid is neutralised with lime, $Ca(OH)_2$, whereby iron hydroxide, $Fe(OH)_3$, and other impurities are precipitated. The liquid is next raised by means of the pump C into the iron settling tank D. From here the clear manganese chloride liquors are run into the *oxidation towers* E,E. These are tall iron cylinders, some 30-40 ft. high and 6-7 ft. in diameter. Steam is blown in so as to raise the temperature of the contained manganese chloride liquors to 55° C., and then the calculated amount of milk of lime is run in from the tank F.

The lime is slaked in the mixer G, thence the fluid mass is run into H and pumped up through the pump J into the lime tank F.

Meanwhile compressed air is blown into the towers E,E, issuing from perforated pipes placed near the bottom of the towers. K is the duplex blower, L the air reservoir, and MM the air conducting pipe. The air is blown through the warm liquid for some four to five hours before the oxidation of the manganese present to manganese dioxide is complete.

The chemical mechanism of the action is not completely understood even after years of research. It seems that first of all the lime, $Ca(OH)_2$, first precipitates manganous hydroxide, $Mn(OH)_2$, thus:—

$$MnCl_2 + Ca(OH)_2 = Mn(OH)_2 + CaCl_2 + H_2O.$$

The $Mn(OH)_2$, a white substance, will take up oxygen spontaneously from the air until it reaches the grade of oxidation Mn_3O_4; however, if excess of lime or NaOH is present, the oxidation will proceed further than this, and the manganese oxide will be oxidised almost completely to the MnO_2 state, forming a black body of composition varying between $CaO.MnO_2$ and $CaO.2MnO_2$, so that the regenerated "Weldon mud" contains chemically united lime (CaO). It is remarkable that, apparently, a trace of $CaCl_2$ solution appears to be necessary before the complete oxidation will take place.

The action is carried out in such a manner that a "mud" containing as little CaO as possible is aimed at. The active component in the mud is, of course, the amount of MnO_2 present, each molecule of MnO_2 present corresponding to the evolution of 2 atoms of Cl.

The progress of the oxidation is followed by withdrawing samples of liquor at frequent intervals and titrating the blackening mud with ferrous sulphate solution and potassium permanganate.

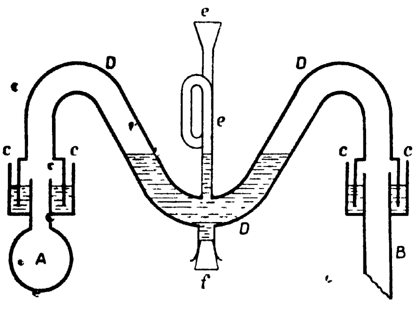

FIG. 2.—System of Connecting the Chlorine Pipes to the Chlorine Stills.

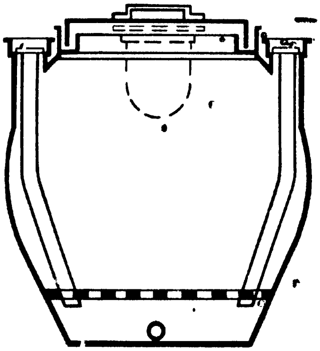

FIG. 3.—Small Chlorine Still.

Towards the end of the action the excess of lime is as far as possible got rid of by running in more manganese chloride solution so long as a precipitate of $Mn(OH)_2$ is caused by the free lime still remaining.

When the process of oxidation is known to be complete the Weldon mud is run out of the base of the towers E,E (by means of the stopcocks N,N) into the settling tank O. The mud settles to the bottom of this tank, whence it is run into the chlorine still A once more, and so used again. The aqueous liquors, principally containing calcium chloride (see equation above), is drawn off from the tank O, and either run to waste or worked up in some other manner.

No less than 70 per cent. of the total chlorine of the hydrochloric acid remains as a waste product in this calcium chloride, a loss of chlorine which causes the Weldon process at the present time only to be worked in those districts where hydrochloric acid does not command a good price, and where the calcium chloride can be utilised.

So far as can be ascertained, the Weldon process is not extending at the present time, the under-described **Deacon Process** (where the waste of chlorine is less), and also electrolytic methods of manufacturing chlorine, steadily gaining ground at its expense (see p. 9). The chlorine evolved from the **Weldon Process**, however, is very concentrated, sometimes amounting to 90 per cent. by volume of the evolved gas.

THE DEACON PROCESS

LITERATURE

See references on p. 3; also

Haber.—"Thermodynamik technischer Gasreaktion." 1905.
Falckenstein.—*Zeit. physikal. Chem.*, 1907, 59, 313; 1909, 65, 371.

The oxygen of the air can be used to oxidise hydrochloric acid to chlorine and water. When a mixture of hydrochloric acid and air is led over a heated suitable "contact" substance the following change takes place:—

$$4HCl + O_2 = 2Cl_2 + 2H_2O.$$

This is the process of Deacon and Hurter. The decomposition, however, is by no means a quantitative one, and the unchanged hydrochloric acid is recovered and used again. The contact substance employed is usually cupric chloride, $CuCl_2$, heated to 450° C. Cupric sulphate, $CuSO_4$, has been used, but is not so efficient as $CuCl_2$.

The action is essentially "catalytic," but it is usually supposed that the $CuCl_2$ is first converted into an oxychloride, which is then, by means of the HCl, reconverted into $CuCl_2$. For example, Hengsten gives the equations:—

1. $CuCl_2 = 2(CuCl_2 + Cu_2Cl_2) + 4Cl.$
2. $2(CuCl_2 + Cu_2Cl_2) = 3Cu_2Cl_2 + 2Cl.$
3. $Cu_2Cl_2 + O = CuO.Cl_2.$
4. $CuO.CuCl_2 + 2HCl = 2CuCl_2 + H_2O.$

Lunge and Marmier come to somewhat similar conclusions, which are, however, denied by Levi and Bettoni, who cannot find in the $CuCl_2$ used any Cu_2Cl_2 or $CuO.CuCl_2$. Moreover, pumice-stone impregnated with Cu_2Cl_2 or $CuO.CuCl_2$ gave between 250°-400° no trace of Cl. Also, $CuSO_4$, chlorides of Ni, Mn, Mg, etc., also strongly heated pumice-stone alone, gave Cl when a mixture of HCl gas and air was led over them. On this ground these authors reject the "oxychloride" theory of the previous writers, and assert that the Cl does not come from the $CuCl_2$ at all, as this latter can be replaced by the SO_4 or substances which do not contain Cl at all, and put forward the suggestion that the catalytic action of these substances is to be referred to the tendency of the substances to form oxychlorides. Levi and Voghera also carried out experiments on the use of catalysers such as $CaCl_2$, $MgCl_2$, $BaCl_2$, $NiCl_2$, $CuSO_4$, CuO, etc.

Ditz and Margosches (D.R. Patent, 150,226, 15th June 1902) have proposed to use as a contact substance the chlorides of the rare earths (Th, Ce, La, Pr, Nd, etc.), which occur as a by-product in the manufacture of thoria for gas mantles. The reaction temperature is 300°-600°. With diluted gases it is stated that the reaction takes place even better than with concentrated 40-50 per cent. gases.

The reaction is reversible, following the ordinary law of mass action:—

$$2HCl + O \overset{\longleftarrow}{\longrightarrow} H_2O \text{ (steam)} + Cl_2 \pm 14{,}700 \text{ calories.}$$

At low temperatures the reaction tends to proceed almost completely in the direction from left to right, with the evolution of heat, but so slowly as to be practically unworkable. As, however, the temperature increases, apparently the attraction of hydrogen for chlorine increases, and the reaction tends to proceed more rapidly in the reverse direction from right to left, so that as the temperature increases the yield of Cl from HCl decreases. Consequently the lower the temperature the greater is the quantity of HCl theoretically converted into Cl_2; but at low temperatures the reaction proceeds extremely slowly, so that it is unpractical to carry it out below 400°-430° C. At a temperature such as 450° C. equilibrium is more rapidly attained, but the yield of chlorine is seriously diminished, and at temperatures much above 450° notable amounts of copper chloride are lost by volatilisation.

The most favourable practical conditions have been worked out by Lunge and Marmier (*Zeit. angew. Chem.*, 1897, 105), who found that the contact substance should be kept between 450°-460° C. Above 460° C. serious losses of copper chloride occur, while below 440° C. the yield of chlorine was bad on account of the slowness with which equilibrium was attained.

As regards the theory of the process the reader should see Haber, "Thermodynamik technischer Gasreaktion," 1905, p. 89. A recent investigation on the equilibrium of the Deacon process has been published by Vogel von Falckenstein, *Zeit. physikal. Chem.*, 1907, 59, 313; 1909, 65, 371-379.

As in all chemical actions where heat is evolved, increase of temperature increases the velocity of the reaction up to a point, and beyond that point the velocity of the reverse reaction increases very rapidly.

It follows, therefore, that as in all chemical reactions attended with the evolution of heat (see the "Contact Process for SO_3 Manufacture," Martin's "Industrial Chemistry," Vol. II.), the *lower the temperature* the more completely does the reaction take place in the direction $2HCl + O \rightarrow Cl_2 + H_2O$, and consequently the more completely the hydrochloric acid is turned into chlorine. Unfortunately, however, at low temperatures the reaction proceeds so slowly as to make it practically unworkable. It is only at 400°-430° that the action proceeds with $CuCl_2$ with sufficient velocity to make the process technically workable. As the temperature increases up to 450°, so also does the rapidity with which equilibrium is attained, although the yield of chlorine per given amount of hydrochloric acid becomes increasingly worse on account of the increasing rapidity of the back action, $H_2O + Cl_2 \rightarrow 2HCl + O_4$. According to Haber, theoretically at 430° C., some 75-85 per cent. of HCl is convertible into Cl, whereas at 577° C. only 50 per cent. is convertible. Possibly some advance may come with the discovery of a more efficient catalytic agent than $CuCl_2$, which works at a lower temperature than 450° C. According to von Falckenstein, the best yield in the Deacon process is obtained by using a mixture of 40 per cent. HCl and 60 per cent. air. About 70-71 per cent. of the HCl gas entering the apparatus can be converted into Cl. On drying the cooled gaseous mixture by passing through concentrated sulphuric acid, and again passing it through the apparatus, a yield of 82-85 per cent. of chlorine can be obtained, while on passing once more through the apparatus, 87-89 per cent. yields are attainable. As regards the influence of *pressure* on the equilibrium, it is a general law that an increase of pressure tends to cause a reaction to proceed in such a direction as to favour the production of products occupying a small volume, as the equation shows:—

$$\underset{4\text{ vols.}\ +\ 1\text{ vol.}}{4HCl + O_2} = \underset{2\text{ vols}\ +\ 2\text{ vols.}}{2H_2O\ (\text{steam}) + 2Cl_2}.$$

An increase of pressure should therefore favour the transformation of HCl into chlorine by the Deacon process, and Foucar (private communication) has suggested that a modified Deacon process carried out under pressure, and at such a temperature as would just prevent the condensation of the steam, would have a future before it.

Fig. 4 shows one of the older forms of the Deacon plant. A is the salt-cake furnace from which the HCl gas is evolved from the action of sulphuric acid on salt. B is a pipe leading off the HCl gases. C is a condenser in which sulphuric acid, aqueous hydrochloric acid, etc., are condensed. E is the preheater, where the entering gases are raised to the right temperature, say 220° C., before entering the contact apparatus F. This consists of a cylindrical iron tower F, surrounded by a brickwork wall *m*, whereby the whole can be heated to the proper temperature (about 430°-450° C.). In the central portions of the tower are piled layer over layer of baked clay or porous earthenware balls, previously soaked in cupric chloride solution and dried. As the $CuCl_2$ is somewhat volatile, the entering gas is first sent through the system from below upwards, after which the direction is changed from above downwards, and so on in alternately reversed directions. By this arrangement loss of copper chloride is minimised.

The German patent, 197,955 (1906), proposes to use the double salt, $CuCl_2.NaCl$, which at 550° is not noticeably volatile. With this salt the gas stream can be heated to 510° C., without much loss of copper, whereas in the ordinary $CuCl_2$, over 460°, a considerable loss of copper occurs.

By means of this system about 65 per cent. of the HCl is, in actual practice, decomposed into Cl. The issuing stream of chlorine-rich gases escapes through the pipe H into a series of cooling tubes J, whence they pass into the tower K, where they meet with a descending spray of water, which washes out the HCl gas, but only absorbs a small amount of chlorine. The aqueous HCl thus obtained is freed from chlorine by blowing through it a stream of air.

From the water tower the chlorine gas next passes into the drying tower L, where it is dried by a descending stream of concentrated sulphuric acid, the dry chlorine emerging at *n*.

In its original form the Deacon process suffered from some grave defects which rendered it unable at first to compete with the Weldon process. The HCl was at first led directly from the salt-cake furnaces into the contact apparatus, and it was found that the latter ceased to work effectively because the unpurified HCl gas carried on sulphuric acid fumes, ferric chloride, arsenic, and dust, which spoilt the contact substance. Hasenclever, of the Rhenania Factory, was the first to make the process really successful. This he achieved by purifying the HCl gas by first absorbing it in water, and then liberated it again in a comparatively pure state by running in concentrated 66° Bé. (107° Tw.) sulphuric acid, and finally blowing air through the liquid. The HCl came over pure in a steady stream, and was led directly into the contact apparatus. This process is still worked on a very large scale.

At Mannheim, in 1909, a further simplification was introduced in the process by obtaining directly in *mechanical salt-cake furnaces* (see Martin's "Industrial Chemistry," Vol. II.) nearly pure HCl gas, free from arsenic, and of a fairly constant strength, consisting, say, of 30 per cent. HCl and 70 per cent. air. This gas is purified by leading it through a series of Cellarius condensers (Chapter VI.), whereby dust and sulphuric acid are deposited. Lastly, the gas is heated to about 220° C., and is led directly into the contact apparatus.

The chlorine evolved in the Deacon process is very dilute as compared to Weldon and electrolytic chlorine. It usually amounts to only 8-12 per cent. by volume, the rest being atmospheric nitrogen and other gases. Consequently, it is difficult to use an ordinary "chamber" for making bleaching powder. The lime must be treated in a special apparatus invented by Hasenclever, which will be described under bleaching powder (p. 46).

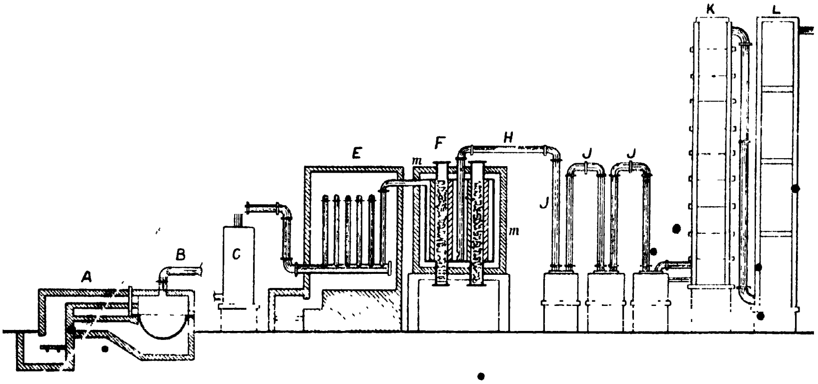

FIG. 4.—Deacon Process of Chlorine Manufacture

The Deacon process is still able to maintain its position and even advance in spite of the growth of electrolytic chlorine. In the Weldon process only about one-third of the chlorine in the HCl is utilised, while in the Deacon process over 40 per cent. of the HCl is transformed into Cl, the rest being recovered as HCl, and, moreover, the oxidation agent, viz., atmospheric oxygen, does not cost anything. The disadvantages of the Deacon process are the trouble in getting the plant to work, the frequent loss of efficiency by the contact materials becoming useless, and the loss of copper by volatilising or otherwise.

Preparation of Chlorine and Hydrochloric Acid from Magnesium and Calcium Chlorides.—Enormous amounts of magnesium chloride, estimated at 500,000 tons, are run to waste at Stassfurt (see Martin's "Industrial Chemistry," Vol. II., "The Stassfurt Industry"), simply because no economic means are known of transforming these mother liquors into chlorine products.

Many attempts have been made to obtain chlorine and hydrochloric acid from magnesium chloride, $MgCl_2$. When the latter is crystallised from its solution it deposits as a snow-white mass containing water of crystallisation ($MgCl_2.2H_2O$).

When this crystallised magnesium chloride is melted it decomposes, forming oxychloride and evolving half its chlorine as HCl, thus:—

$$2MgCl_2 + H_2O = MgO.MgCl_2 + 2HCl.$$

If now the magnesium oxychloride remaining behind is heated in a stream of steam nearly all the chlorine is evolved as HCl, leaving magnesia, MgO, behind, thus:—

$$MgO.MgCl_2 + H_2O = 2MgO + 2HCl.$$

This is a method of obtaining HCl from $MgCl_2$ which has actually been put into practice, but without much success.

In order to obtain chlorine from magnesium chloride or oxychloride the substance must be ignited in a stream of air when it evolves chlorine, but only incompletely; it does not melt, but remains porous. This, essentially, was the Weldon and Pèchiney process, worked for a time, but unsuccessfully, at Salindres in S. France, the magnesium chloride being obtained by concentrating the mother liquors left after crystallising out the salt, NaCl, the manufacture of salt being here a considerable industry. Similar processes were worked at Neustassfurt and Leopoldshall in Germany, two manufacturers of potassium salts seeking to utilise the magnesium chloride waste liquors in this manner, but again with no success at Neustassfurt. In Leopoldshall the manufacture of chlorine by this process was given up in 1909, after being worked since 1890, but hydrochloric acid is still obtained at the latter place by the following method:—

Powdered magnesia, MgO, is mixed with the concentrated $MgCl_2$ mother liquors, when combination ensues, with the formation of solid plates of magnesium oxychloride, containing, roughly, 10 per cent. MgO, 40 per cent. $MgCl_2$, and 50 per cent. H_2O. These plates are then stacked up side by side and one over the other in the shaft of a furnace, care being taken to suitably support the plates. From beneath, the hot gases from the furnace stream through the mass and heat them to a red heat. The plates, shrinking and subsiding downwards, as they do in the hotter parts of the furnace, yield up most of their chlorine in the form of dilute HCl gas, which is then condensed and absorbed in the usual way by passing the furnace gases up absorbing towers, where they meet with a stream of descending water.

The firing of these furnaces is "brown coal," which gives off much water, and so aids the action of the heat in causing the complete decomposition of the oxychloride. The resulting HCl solution is very dilute, only 15° Bé., but has the great advantage of being practically arsenic free.

There finally remains a calcined mass containing 15 per cent. $MgCl_2$ and 85 per cent. MgO which is then ground up and utilised, partly for mixing with the $MgCl_2$ liquors for repeating the process, and partly for the production of magnesium oxychloride cements (sorel cement, xylolith) which is now being used in increasing quantities for floorings, artificial marble, etc. (see p. 85).

There seems, however, but little prospect of an increased production of HCl from this or allied methods, as the ease and abundance with which HCl is produced by the extension of the salt-cake furnace methods puts the former out of court unless the running costs can be considerably reduced.

As regards the production of HCl and Cl from **calcium chloride**, this is one of the grea problems of the day. By the ammonia soda process enormous amounts of waste calcium chloride liquors are produced, and also by the Weldon recovery process, and the manufacture of $KClO_3$ Enormous numbers of proposals, almost always devoid of practical success, have been made to manufacture Cl cheaply from $CaCl_2$, or to utilise this chlorine effectively; *e.g.*, Solvay in 1877 1888, and 1889 took out a number of patents which consisted in heating $CaCl_2$ with sand, clay etc., under various conditions in a stream of air (see "Chemische Industrie," **1**, 49 (1878), and Hurter, *Journ. Soc. Chem. Ind.*, **2**, 103 (1883)). An account of the various proposals is given in Lunge's book, "Sulphuric Acid and Alkali," Vol. III.

CHAPTER II

Electrolytic Chlorine and Alkali

CHAPTER II

ELECTROLYTIC CHLORINE AND ALKALI

LITERATURE

ALLMAND'S "Principles of Applied Electrochemistry." 1912.
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V. ENGELHARDT.—"Hypochloiite u. Elektrische Bleiche" (1903); also *Chemiker Zeitung* (1911).
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L. FORSTER.—"Elektrochemie wasseriger Lsgn." 1905.

WITHIN the last two decades a large industry has arisen out of the electrolysis of the alkali chlorides, whereby not only chlorine, but also valuable bleaching solutions, chlorates, and caustic alkalies are obtained. At the present time it is stated that over half the world's supply of chlorine and chlorine products arises out of the electrolysis of the alkali chlorides. A large number of different processes have been proposed, but we will only mention those which have been attended with some success.

General Principles.—When an electric current is passed through a salt solution the positively charged metallic ions pass to the negative electrode (cathode), whereas the negatively charged chlorine ions pass to the positive electrode (anode) thus:—

$$\mathrm{NaCl} = \underset{(\text{to} - \text{pole})}{\overset{+}{\mathrm{Na}}} + \underset{(\text{to} + \text{pole})}{\overset{-}{\mathrm{Cl}}}.$$

Arriving at the electrodes, these charged ions give up their electrical charges, and the sodium ions become ordinary sodium, which at once reacts with the excess of water present, to yield H gas, and produce caustic alkali, thus:—

$$2\mathrm{Na} + \mathrm{H_2O} = 2\mathrm{NaOH} + \mathrm{H_2},$$

so that at the cathode caustic soda accumulates and free hydrogen is given off. On the other hand, the chlorine ions, after giving up their negative charges at the + pole, are liberated as chlorine gas at the anode (+ pole), and also remain dissolved in the liquid surrounding the anode. In very dilute solutions, and with too high electrical potentials, the water suffers electrolysis, oxygen coming off at the positive pole, and hydrogen at the negative.

The conduction of the current across such an electrolytic solution depends upon its transportation by the charges on the ions. Thus every equivalent ion, *e.g.*, 1 g. of hydrogen, 35.5 g. of chlorine, 24 g. of sodium, etc., carries with it the same quantity of electricity, viz., 96,540 coulombs—either positive or negative electricity, according to the + or − character of the ion (Faraday's law). It is therefore an easy matter to calculate the amount of chemical products theoretically producible by the passage of a certain quantity of electricity through a liquid. *E.g.*, to produce, say, 35.5 g. of chlorine, or 40 g. of NaOH (from 23 g. of liberated Na) we theoretically only require the passage of 96,540 coulombs.[1] Theoretically, a current of one ampere liberates in one hour 1.3236 g. of chlorine. In practice, however, side or secondary reactions diminish the yield of these products.

To liberate any ion a definite electrical tension is required, measured in volts. And to drive a current continually through any electrolyte there is thus required a definite voltage depending upon the nature of the ions liberated. These are the so-called "polarisation" voltages, which must be overcome before the ion gives up its electrical charge and is liberated.

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[1] A coulomb is the quantity of electricity represented by one ampere flowing for one second past any section of a circuit.

The total amount of *electrical energy* required for electrolysis is measured by the product of the current in amperes, and the voltage at which it is forced through the liquid, the unit being called a volt-ampere. 1 volt-ampere = 1 watt/second = 0.24 gramme calorie.

For electrolysis, Ohm's law takes the form:—$C = \frac{E - e}{R}$, E being the voltage of the source of electricity, and e the polarisation voltage which must be overcome before the current will flow through the electrolyte at all. It is always possible to calculate *approximately*, from the heats of combination of component salts, the reactions which take place. Thus, confining ourselves to the electrolysis of NaCl solution, we have the equations:—

$$NaCl + H_2O = NaOH + H + Cl$$

$$\begin{array}{rl} NaCl = Na + Cl & - 96{,}400 \text{ calories} \\ Na + H_2O = NaOH + H & + 43{,}400 \text{ calories} \\ \hline \text{Difference} & - 53{,}000 \text{ calories.} \end{array}$$

Hence, in order to decompose 1 g. mol. of NaCl (58.5 g.) and liberate 40 g. NaOH, 1 g. H and 35.5 g. Cl, we require the expenditure of energy represented by 53,000 calories, which is equivalent to 53,000/0.24 = 220,800 volt-amperes. Now 96,540 coulombs = 96,540 ampere-seconds are required to liberate the gram equivalent of these quantities, and so the *minimum* voltage (assuming that all the heat is represented by electrical energy) necessary for decomposing the solution is 220,800/96,540 = 2.3 volts.

As a matter of fact, however, in practice a much greater amount of energy than this is usually required. Thus a considerable voltage is required to drive the electric current against the high resistance of the electrolyte, and this causes the generation of much heat, which is derived from the electric current.

Consequently, in order to pass a current of any intensity across the liquid, we must work with a voltage considerably greater than this minimal voltage of 2.3 volts. As the frictional heat represents a waste of electrical energy, in practice the resistance of the electrolytic cells is diminished to the greatest possible extent by making the electrode surfaces as large as possible, and the layer of electrolyte between them as short as possible. Moreover, the voltages are kept as low as possible, the conditions for economic production being low voltages and currents of great strength. In order to render the salt solutions good conductors (and so save waste of electrical energy in frictional heat effects) they are made as concentrated as possible, and usually are hot.

As regards the source of power for generating electricity, this is usually and most cheaply provided by water power, and so the Niagara Falls in America, Norway, and other countries rich in water power are the main seats of this new industry.

However, where water power fails (as in Germany) the power is often provided from coal, brown coal, peat, the producer gases evolved in some furnaces, and coke ovens, etc.

The currents are usually generated by water turbines driving dynamos, and the current is delivered to the salt solutions at a definite voltage and a definite current density, such as experience shows is best for the particular cell employed. These cells are small, and the current is often divided among hundreds, and sometimes thousands, of individual cells (as these latter cannot be greatly enlarged to meet increased power, as is the case in most other industrial plants).

ELECTROLYSIS OF ALKALI CHLORIDES FOR PREPARING CHLORINE AND ALKALI

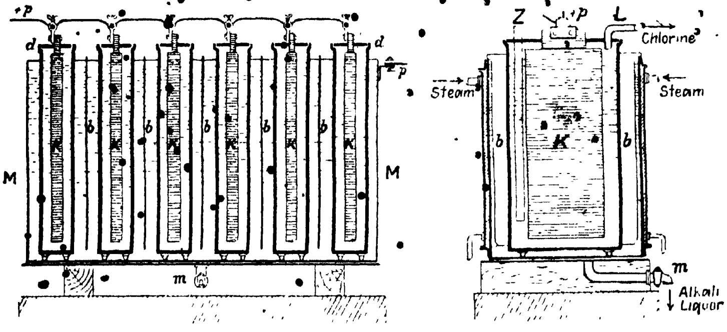
Four main processes are worked, namely:—(1) The diaphragm process, (2) the mercury process, (3) the Bell process, (4) the fused electrolyte process. We will describe each in detail.

(1) **The Diaphragm Process.**—The earliest and most successful cell of this type is the Griesheim, which has been worked (*Chemische Fabrik Griesheim-Elektron*) since 1890. Large works employing this cell also exist at Bitterfield, Basel, and the Badische Anilin- und Soda-fabrik also use this process. The cell (Figs. 5 and 6) consists of an iron box MM, which is made to serve as the cathode. Inside this are placed six small porous cells *d,d*, serving as diaphragms in which dip the anodes K,K,K, all connected in series, the whole being filled with *saturated NaCl solution.*

The walls of the small porous cells *d,d*, (diaphragms) are a composition of cement, NaCl and HCl (Breuer, German Patent, 30,222, 1884). In the course of use the NaCl dissolves and leaves an extremely fine-pored wall, which separates the anodic from the cathodic space, and which allows the current to pass through. This composition has proved very resistant against alkali and chlorine. The anodes KK, dipping into each porous cell, are now made of magnetic iron oxide (Fe_3O_4) fused in the electric furnace at 2,000-3,000° C., and poured into moulds. Such electrodes have proved superior to the carbon poles previously employed, which are attacked by nascent oxygen.

Separating each small porous cell are iron plates *b,b*, going right across the main iron box, MM, and dipping nearly, but not quite, to the bottom. These iron plates form (together with the iron walls of the main box MM) the cathodes.

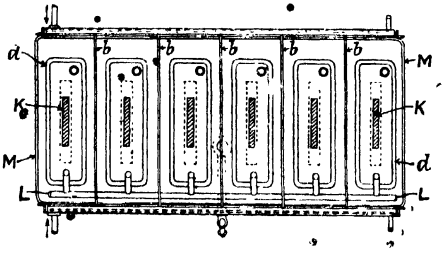
The porous cells surrounding the anodes are covered with lids, chlorine escaping through a tube leading from the interior porous cells as shown at L, the anodes passing right through the lid. The chlorine is led away through an earthenware pipe to the chlorine chamber.



Longitudinal Section. Cross Section.

FIG. 5.—The Griesheim Cell.

Also each cell is provided with a tube-shaped grid of earthenware for filling in salt, thus keeping the solution saturated. The bath MM is also provided with a lid through which the evolved hydrogen escapes. This gas is either led into



Ground Plan.

FIG. 6. The Griesheim Cell.

a gasometer or it is led away to the pumps, and compressed in strong steel cylinders under 150 atmospheres pressure, and stored in this form.

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[*] The following are the changes which occur in the cell when the current is passed through the saturated NaCl solution in the bath. The Cl ion passes through the diaphragms *d,d* into the anodic space and there escapes as Cl gas, while the Na ion passes from inside the diaphragm and discharges itself on the cathodic space outside, being converted into NaOH and H, which escapes as above described. As the action proceeds the solution becomes weaker and weaker in NaCl, so that saturated NaCl solution is run in through the pipe Z, and the solid salt added from time to time also maintains the supply of salt to the liquid. Consequently in the cathodic space there gradually collects NaOH liquors mixed with a dilute NaCl solution, and this is run out from time to time by means of a tap M, the deficiency being replaced by fresh NaCl solution entering through Z, so that there is a continuous flow of electrolyte through the system. The action, however, does

not proceed to completion. As soon as NaOH is formed it begins to itself take part in carrying the current, the tendency becoming the more marked the more NaOH that is present. It is supposed that the NaOH decomposes electrolytically, thus:—

$$2NaOH = 2Na + 2(OH)'.$$

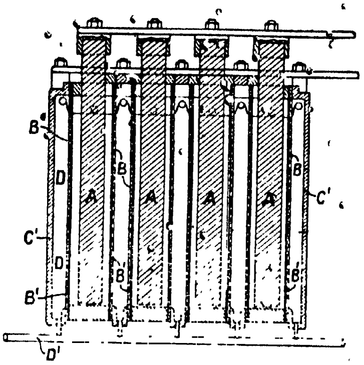

FIG. 7.—The Hargreaves-Bird Cell.

The Na ion at the cathode then gives up its charge, and reacts with the surrounding water to produce NaOH again and H$(2Na+2H_2O=2NaOH+H_2)$, while at the cathode we get the OH' ions similarly changing into water and oxygen $(2(OH)'=H_2O+O')$, so that the net results are that hydrogen is given off at the cathode and oxygen at the anode, and a considerable amount of the current is used up uselessly simply in decomposing water. To prevent this waste, therefore, in practice the process of electrolysis is stopped as soon as about one-third of the NaCl has been changed into NaOH, and the NaOH liquors formed, containing about 75 g. NaOH, and 160-200 g. NaCl per litre, are run off into vacuum evaporators and concentrated.

With the object of diminishing as much as possible the internal resistance of the cell, the polar surfaces are made as large as possible, and brought as close as possible together, while the salt solution is maintained at 80°-90° by means of a steam jacket.

It has been found that the best results are attained in practice by using a voltage of 4 volts to drive the current across the path, the current density being 100-200 amperes per square metre. Since the equivalent amount of products liberated are 35.5 g. Cl + 40 g. NaOH + 1 g. H, by the passage of 96,540 coulombs (*i.e.*, ampere-seconds) through the liquid, with 4 volts driving this current the energy expended per second would be 4 × 96,540 volt-amperes = 525 H.P. In other words, 525 H.P. working for 1 second would yield 35.5 g. of Cl, or 1 H.P. working for twenty four hours would give 5.85 kg. of Cl = 16 kg. of bleaching powder = 6.6 kg. NaOH = 0.17 kg. H (= 2 cub. m.).

It should be pointed out that when the chlorine formed comes into contact with the NaOH produced we get, in the cold, some sodium hypochlorite produced; in the hot solution, however, sodium chlorate is produced. So that the NaOH produced sometimes contains small amounts of hypochlorite and chlorate. The hypochlorite and chlorate in the liquors tend to attack the carbon anodes, producing CO_2, which is absorbed by NaOH forming carbonates. So that wherever carbon electrodes are used, small amounts of carbonates are usually found in the resulting NaOH.

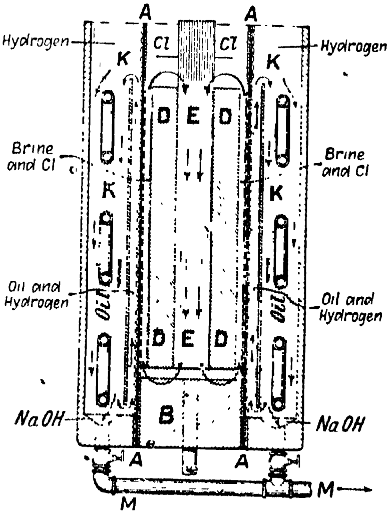

FIG. 8.—The Townsend Cell.

The Hargreaves-Bird Cell[1] is used directly for the electrolytic production of sodium carbonate. The construction of this cell is best understood by reference to Fig. 7. A,A are carbon anodes dipping into a saturated solution of NaCl contained in the anodic cells BB', B'B. The walls of these cells are made up of porous diaphragms, consisting of cement or some similar material, to which is affixed on the *outside* a network of iron gauze, which forms the cathode. The NaCl solution flows into the anodic space through a tube near the top, and pours through the diaphragm surrounding the anode, out through the wire gauze into the exterior empty space DD, finally escaping through the tube D′; as the salt solution pours through the cell, subjected to the powerful electrolytic action by the current passing from A to B′, and consequently the salt solution emerges through the diagram into the exterior empty space DD, it is largely decomposed into NaOH. In DD, however, it meets with a stream of steam and CO_2, which immediately combines with the NaOH to form Na_2CO_3, which pours off through D′. The exterior space DD thus remains empty. The Na_2CO_3 liquor is gradually evaporated and the crystallising Na_2CO_3 separated by centrifugals.

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[1] See C. Kershaw, *Electrical World*, 46, 104; English Patents, 18,871, 1892; 5,197, 1893; 18,173, 1893.

According to Kershaw, the main cells are 10 ft. long by 5 ft. 14 in. deep, and are united in batteries of fourteen. The brine is pumped directly from the salt springs into the battery, and a current of 2,000 amperes, under a tension of 4-4½ volts, is passed through the liquid. Every cell decomposes 100 kg. salt in twenty-four hours. Current efficiency, 90 per cent. The escaping Na_2CO_3 liquors contain 150 g. Na_2CO_3 per litre. About 66 per cent. of the NaCl is decomposed into NaOH.

This process is worked by the Electrolytic Alkali Company in Middlewich, but the success in England does not appear to be very marked, although the plant appears to be more successful abroad, where electrical power is cheaper.

The **Townsend Cell** (Fig. 8) consists of an interior diaphragm of porous material, *i.e.*, asbestos mixed with iron oxide and hydroxide, firmly fixed into a non-conducting cement foot B. Surrounding and in close contact with the porous diaphragm AA is the cathode, made of *iron gauze*. Into the interior of the diaphragm projects the hollow anode (of Acheson graphite) DDDD, which nearly fills the entire central space. Through the middle of this anode is a tube EE, down which a strong NaCl solution is pumped. This NaCl, as it passes between the wire gauze cathode on AA and the anode DD, is subjected to the powerful electrolytic action of the strong current flowing between them. The NaOH formed streams through the diaphragm AA into the exterior space KK, which is filled with oil, which serves as the inactive fluid which separates the cathodic and anodic fluids and prevents them uniting. The NaOH liquors sink below the layer of oil to the bottom of the space KK, and are run off through MM. The oil bath can have its temperature regulated by closed steam or water coils. Cl escapes from the anodic space and H from the cathodic space (see English Patent, 18,403, 1904).

According to Backland (*Chemiker Zeitung*, 1909, **33**, 1125), at Niagara Falls a current of 2,500-5,000 amperes is sent through a battery of seventy-six cells. The "density" of the current used is about 1 ampere for each square inch anodic surface. The voltage per cell is 4. The diaphragms are cleaned every thirty days. Current efficiency, 90 per cent. 15-20 l. of NaCl solution are sent through each cell per hour. The liquors escaping contain 150 g. NaOH and 200 g. NaCl per litre.

The main advantage of the process is stated to be the almost complete absence of chlorates and hypochlorites in the escaping liquors. The resulting NaOH liquors are evaporated, separated from the NaCl (which crystallises out), again evaporated in open boilers, and sold containing 76-77½ per cent. NaOH, together with 2 per cent. Na_2CO_3, and a small amount of NaCl.

Le Sueur's Cell, of latest construction, is described in the American Patent, 723,398. The cell (Fig. 9) is divided into two compartments by the diaphragm AA (made of asbestos), which is coated with *iron gauze*, which forms the cathode. A carbon *anode* B passes through a lid closing the anodic compartment C. A stream of NaCl solution enters through the pipe *e*, enters the anodic compartment C by means of a hole bored in the lid, and then flows out through the diaphragm into the cathodic compartment D. The electrolysed brine collects in D, and the resulting liquor, rich in NaOH, escapes through F. The fluid pressure in C must be greater than in D, otherwise the liquid will not escape readily through the diaphragm.

A modification of this process is stated to be worked at Rumford Falls in Maine (U.S.A.).

The **Outhenin-Chalandre Cell** (see *Moniteur Scientif.*, 1907, **789**, 586) has been used extensively in France, Switzerland, Italy, and Spain. The anodes are of graphite, the cathodes of iron, and the diaphragm consists of a special kind of porous earthenware.

The **Billiter-Siemens Cell** (see British Patent, 7,757, 1907; Kershaw, *Journ. Soc. Chem. Ind.*, 1913, **32**, 993-995; Allmand, *loc. cit.*; Allmand, "Principles of Applied Electrochemistry") has, since 1907, been extensively introduced on the Continent and at Niagara Falls.

The apparatus (Fig. 10) consists of a bell (11) closed at the bottom by a diaphragm (1, 2), which rests on an iron or nickel net (3), which serves as the negative cathode. Inside the bell is the anode (8) (made of carbon), the whole standing in an outer vessel (10).

The special feature of this cell is the nature of the diaphragm. The wire net cathode (3) is covered with ordinary commercial asbestos cloth (1), *on which is piled a powder diaphragm* (2), made of a composition consisting of an insoluble powder (like barium sulphate or alumina), with asbestos wool, the whole being made into a tenacious but consistent mass with a solution of common salt.

NaCl solution enters through the pipe (12), flows right through the diaphragm, is subjected to electrolysis in so doing, and escapes as NaOH through the outlet (13).

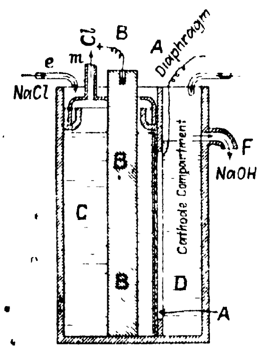

Fig. 9.—The Le Sueur Cell.

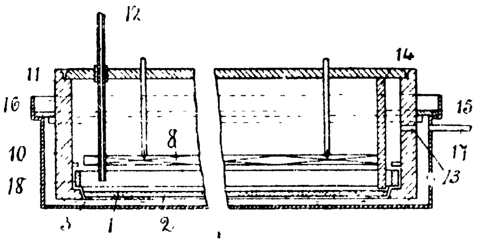

Fig. 10 The Billiter Siemens Cell.

The cell is provided with a special heating arrangement, which serves to keep the liquid hot.

With 4-5 volts the apparatus gives 12 per cent NaOH, with efficiencies of 90-95 per cent. of the theoretical amount. Cl gas of 90 per cent strength is evolved. An apparatus with a cathodic net of 1 sq. metre working under a tension of 4-4.5 volts requires a current of 600 amperes. The salt solution is maintained at 60° C. Anodes of magnetic iron oxide are now stated to be used instead of carbon.

The **Billiter-Leykam Cell**, a modification of the Billiter Siemens cell, is an improved form of the bell jar cell, using cathodes hooded in asbestos and placed underneath the anodes.

Working at 85° C., it furnishes a 12-16 per cent. NaOH at a current efficiency of 92 per cent., using 3.2 volts and employing unpurified brine. The drawback is the small amperage per unit of floor space.

The **Finlay Cell**, described in the British Patent, 1,716 of 1906, also in Allmand's "Principles of Applied Electrochemistry," p. 380, is a double diaphragm cell, with a doubly counter-flowing electrolyte traversing the cell from end to end by means of tubes. By means of a filter press arrangement (the cell being built much like a filter press), the thickness of the electrolyte is reduced to a minimum. There is a constant difference of hydrostatic pressure at every point of the diaphragm, so that uniform percolation of the brine is secured.

Fig. 11 shows a section of a battery of cells. *a,a* are the anodes, *b,b* the cathodes, *d,d* the diaphragms (made out of asbestos plate, with holes therein at top and bottom for allowing brine to flow through according to a definite counter-current circulating tube system), and *p,p* are "distant pieces" (*i.e.*, frames placed between the diaphragms) which, when pressed up by the screw 31-32, enclose a space which constitutes an electrolytic chamber. These distance pieces are also provided with holes, which, with the corresponding holes in the cathode, anode, and diaphragms, constitute parts of the tubes of the circulating system. When these parts are arranged in the cell as shown, and are pressed together between the end plates 30 by means of the screw 31, and the handwheel 32, orifices in the cathodes, diaphragms, distance pieces, and anodes all coincide, and form continuous tubes or ducts for circulating the electrolyte. 36 is the feed system for the brine, 37 and 38 are, respectively, out-flow cisterns for the products of the cathode and anode chambers respectively. 39 is a separator for H gas, a similar separator (not shown) being employed for the chlorine.

The separators and pipes connect with the three double lines of holes in the elements, making up the battery, so that three continuous tubular circuits are formed for the flow of liquids.

According to Donnan (*Journ. Soc. Chem. Ind.*, 1913, **32**, 994) this cell, working with purified brine and a current density of 4 amperes per square decimetre of diaphragm, can produce 8-12 per cent NaOH at a voltage not exceeding 3·5 volts, and with a cathodic current efficiency of 98-99 per cent.

In 1913 three 1,000 ampere units were being satisfactorily operated in Belfast. The Finlay cell, however, according to Kershaw (*loc. cit.*), is handicapped by the low concentration of the NaOH produced.

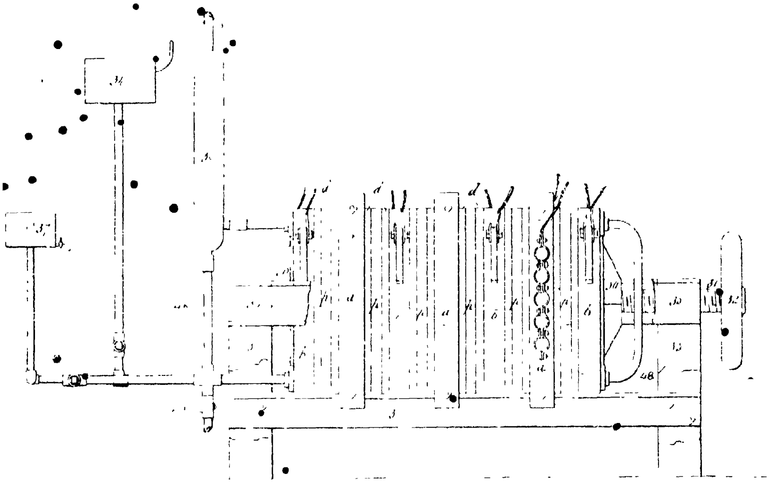

FIG. 11.—The Finlay Cell.

Kershaw (*loc. cit.*) states that diaphragm cells, with a moving electrolyte, the flow of which through the cell counteracts the effects of convection currents and of ionic migration which are constantly occurring, are now the most efficient type of electrolytic cell for the production of alkali and chlorine compounds, the Billiter Siemens and Finlay cells possessing the highest energy efficiencies.

The following figures are given, showing the current and energy efficiencies of the various electrolytic alkali processes:—

Name of Process or Cell.	Efficiencies per Cent. Current	Efficiencies per Cent. Energy.	Concentration of Soda Liquor.
Griesheim	75	48	[illegible]·2 N
Hargreaves-Bird	80	54	
Townsend	94	4[illegible]	4 N
Billiter-Siemens	[illegible]2	68	3 N
Billiter-Leykam	95	59	3·4 N
Finlay	98	75	2 N
Castner-Kellner	91	52·3	...
Aussig "bell"	87½	40·9	

Note.—A concentration of 1 N is equivalent to 40 g. of NaOH per litre.

(2) The Quicksilver Process of Electrolysing Alkali Chlorides.—In this process quicksilver serves as the cathode, taking up the liberated Na as an amalgam, and giving it up at another place to water to form NaOH and hydrogen. The great advantage of this process is that the NaOH formed in the neighbouring cell is completely chlorine free, and on evaporating the solution a very pure NaOH is obtained. Moreover, it is possible to prepare directly very concentrated NaOH liquors, so that not such a great deal of evaporation is necessary as in the process first discussed. The absence of a diaphragm greatly reduces the resistance, and so allows the whole operation to be carried out at a low voltage. The main disadvantage is the great cost of the large quantities of quicksilver required for the plant.

Fig. 12 shows the cell employed by the **Castner and Kellner Co.,** Weston Point, Runcorn. The large trough MM is divided into three compartments A,B,A, by two partitions which do not touch the bottom of the cell, but fit into grooves at the bottom. Two stout graphite electrodes project through the walls of the two outer compartments of the vessel, while the middle compartment is fitted with an iron grid to form the cathode (−pole). The non-porous massive partitions do not reach quite to the bottom of the cell, but dip into a layer of mercury covering the bottom as shown. A solution of alkali chloride flows through the two outer compartments, and water through the middle compartment.

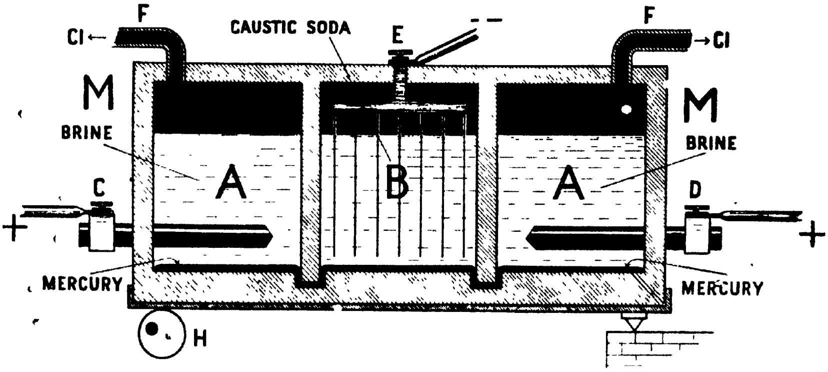

FIG. 12.—The Castner-Kellner Cell.

On passing the current, the salt dissolved in the water of the two outer compartments A,A is split up into Cl and Na ions. The chlorine is evolved as such at F, but the sodium travels with the current and dissolves in the mercury at the bottom of the compartment, forming sodium amalgam. A slow rocking motion is given to the whole apparatus by means of an eccentric wheel placed at H, and this makes the mercury flow from one compartment into the other, and so brings the mercury amalgam into contact with the water in the middle cell, where it is decomposed, forming NaOH, evolving H, and regenerating the mercury. The hydrogen escapes through the loosely-fitting cover. When the NaOH formed in the middle compartment is sufficiently concentrated it is run off into another tank for boiling down.

According to W. Gordon Carey (*Journ. Soc. Chem. Ind.*, 1913, **32**, 995), 144 cells of the rocking Castner type, measuring 6 ft. by 4 ft. internally, and containing 200 lbs. of mercury, gave with a current of 550 amperes at 4 volts (using Acheson graphite anodes and iron cathodes) per cell about 0.75 gall. of 20 per cent. caustic soda per hour. Mercury in the cells was purified from disintegrated graphite by mechanical means and dilute nitric acid, the total loss of mercury being under 2 per cent. per year. The evolved chlorine made 40 tons of bleaching powder per week. In working the cells care has to be taken to prevent undue hydrogen formation in the anodic chamber (the gases being repeatedly analysed), otherwise explosions may occur. Kershaw (*loc. cit.*) gives the current efficiency as 91 per cent. and the energy efficiency 52.3 per cent. See also Lepsius (*loc. cit.*) and English Patents, 16,046, 1892; 10,584, 1893.

Solvay-Kellner Cell.—Fig. 13 shows a diagram of the Solvay-Kellner cell.

The carbon anodes A, A, A, A are joined up as shown, and dip into a strong solution of brine which fills the trough XY, the brine entering at S and flowing out at S¹. Simultaneously a stream of mercury enters at B, flows along the bottom of the cell and escapes at D, flowing over a "weir" at C. As the current passes from the carbon electrodes to the mercury, the sodium dissolves in the mercury to form amalgam, which is then removed at D, decomposed by steam, forming H gas and NaOH, and the recovered mercury is pumped in again at B. Chlorine escapes continually at F The apparatus is thus a continuous working one. The escaping amalgam contains usually 0.2 per cent. of Na. The cell can be built in very large units, taking 10,000-15,000 amperes (see German Patent, 104,900, 1898).

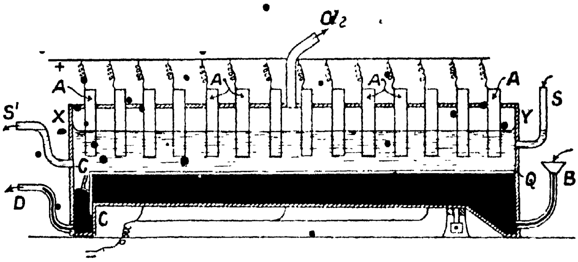

FIG. 13.—The Solvay-Kellner Cell.

Rhodin's Cell, stated to be in use in Sault Ste Marie in Canada, consists (Fig. 14) of a circular iron trough AA, in which is placed a bell-like vessel BB, through which passes a series of carbon anodes D, D. The NaCl solution is contained in the bell. The exterior trough AA, however, is filled with water, and the bottom of the trough contains mercury, which forms the anode. The whole bell slowly revolves, and the quicksilver absorbs the liberated Na as sodium amalgam, which is then decomposed by the water in the exterior trough, forming NaOH and H (see *Zeit. f. Elektrochem.*, 1903, 9, 366; also German Patent, 102,774, 1896).

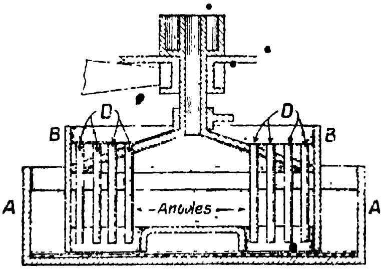

FIG. 14.—The Rhodin Cell.

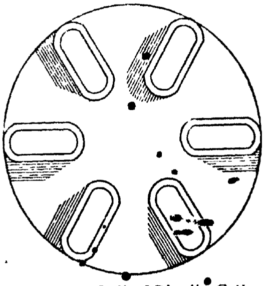

FIG. 15. -Bell of Rhodin Cell, as viewed from below.

The advantages of the mercury cell are (Lepsius, *loc. cit.*):—(1) Very pure caustic alkali of high concentration; (2) high current efficiency; (3) no oxygen evolved. The disadvantages are:—(1) High voltage required (4.3 volts); (2) cost of mercury (72 tons per plant of 6,000 H.P.); (3) expense of first cost (apart from Hg).

(3) **The Bell Process.**—In this process no diaphragms are used, the separation of the liquors being made dependent upon the superior specific gravity

of the caustic soda or caustic potash solution, which then sinks to the bottom, leaving the NaCl or KCl solution above.

Figs. 16, 17, and 18 show the **Aussig-Bell Process** in longitudinal and in cross section (see German Patent, 141,187, 1900). Here the anode is enclosed in an inverted, non-conducting bell, with the cathode outside. In a vessel w stand some twenty-five small inverted earthenware "bells," G,G, coated externally with iron sheeting *ee*, which forms the cathodes. Inside each bell is a carbon anode A, placed so that only a small space is left between the walls of the bell and A. All the bells are connected in parallel, as shown in Fig. 17. Through an opening *c* in the carbon anode A a saturated stream of NaCl slowly pours out of many small holes in the pipe *dd* into the cell. As it enters, the liquid is subjected to the action of the electric current, and the heavy caustic soda formed sinks downwards and fills the trough beneath; as it does so, it is continually removed by the overflow pipe *i*. The Cl gas escapes out of F. The openings B,B in the bells are used for connecting together the gas spaces of the twenty-five small bells, so as to maintain internal gaseous pressure the same in each cell.

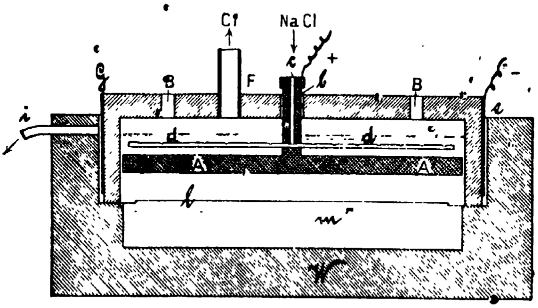

FIG. 16.

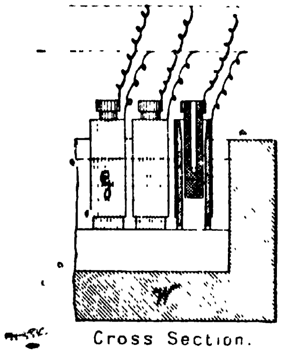

FIG. 17.

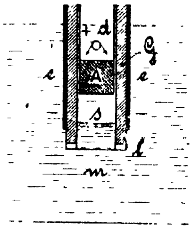

FIG. 18.

The Aussig-Bell Cell.

The theory of the process has been worked out in detail by O. Steiner (*Osterr. Chem. Zeit.*, 1907) and F. Chancel (*C.R.*, 1908, 1789). "The alkaline cathodic liquors form in the "bell" sharp layers (Fig. 18), the definiteness of which must be maintained if the process is to work efficiently. Its position in the cell, also, must not be altered to any great extent, a state which can only be maintained by continuous working. For in the process of electrolysis, the neutral zone, if left to itself, would steadily advance upwards in consequence of the passage of OH ions toward the anode, for, as explained on p. 16, as soon as any KOH is formed, it begins to take part in the electrolysis, the K passing towards the cathode and the OH ions towards the anode; and it is obvious that in the cathodic liquors, where excess of KOH is present, it is the KOH which is for the greater part electrolysed, whereas in the anodic solution above it is the KCl which mainly undergoes electrolysis. Consequently, if we were dealing with a stationary fluid, the KOH layer would steadily creep upwards towards the anode, and this is only prevented by a steady continuous feed of KCl solution at such a rate as to just counterbalance the rise of the KOH layer, so that the "neutral zone" remains in a stationary condition in the cell, neither advancing up the bell nor receding below it—conditions which are easily maintained by carefully regulating the voltage and temperature, and the inflow of KCl solution, so as to maintain equilibrium. The neutral layer must remain several centimetres distant from the anode, and the liquid should not be heated to any great extent.

The iron cathode must be close to the bell, and the anode must be perfectly horizontal.

It has been found that the necessary voltage for efficiently working this process is 4-5 volts, while the current-efficiency is given as 85-90 per cent. It yields alkaline liquors containing often 120 g. KOH per litre—consequently much richer in KOH than the liquors obtained by the diaphragm process. However, the electrolysis of the KCl cannot be carried to completion owing to the growing yield of O together with the Cl, also some chlorate is formed.

One disadvantage of the apparatus is the smallness of its dimensions,[1] and the care and exactness with which it must be regulated, one necessary condition to this being exact horizontalness. Once in action, however, it will keep long at work (the graphite anodes having, it is stated, a life of five years), and requires but little supervision.

(4) The Fused Electrolyte Process is stated to be successfully worked on the Niagara Falls (see Haber, *Z. Elektrochemie*, 1903, 9, 364), and is protected by the English Patents, 6,636 and 6,637 of 1898, and by the German Patents, 117,358, 118,049, 118,391, 119,361. It is usually known as Acker's process. Molten lead is used for the cathode for collecting the sodium, and the resulting alloy of lead and sodium is then decomposed by steam to form hydrogen and sodium hydroxide. Fig. 19 shows the apparatus. Four graphitic anodes A, A, A, A dip into a 12-15 cm. deep bath of fused salt, so that they are only separated by a distance of 2½ cm. from the cathode of molten lead C, and on which the molten NaCl floats. The molten lead is contained in a vessel built up of fire-resisting material, the component parts of which are kept fastened securely together without mortar or cement merely by the molten salt penetrating between the crevices, and there solidifying, forms the binding material.

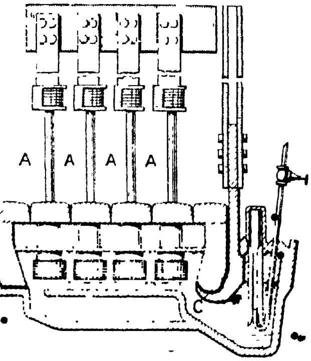

Fig. 19. The Acker Process.

A powerful current of 8,000 amperes, under a tension of 7 volts, the current density being 2.9 amperes per square centimetre area, keeps the bath in a molten condition, the lead taking up some 4 per cent. of Na, and being then run off and decomposed by a blast of steam under a pressure of 2-3 atmospheres. This regenerates the lead, which is pumped back into the furnace again, while a stream of burning H escapes; above the lead the NaOH forms in a layer, which steadily runs off (about 11 kg. in one hour) and is absorbed in special vessels. The chlorine, mixed with air (10 per cent. Cl to 90 per cent. air), escapes from the anode and is conducted to the *Hasenclever bleaching powder apparatus* (p. 46) for chlorinating lime.

Although at least 50 per cent. more energy and a higher voltage is needed with this process than for the electrolysis of aqueous solutions, yet this is to some extent compensated by the high yield and concentration of NaOH, averaging 94 per cent. The impure salt is directly converted into NaOH, which is then fused in iron boilers in order to remove traces of MgO and CaO, which are derived from the Ca and Mg salts originally in the salt. The MgO and CaO settle out at the bottom, the resulting products consisting of 97.4-97.6 per cent. NaOH and 1 per cent. Na_2CO_3.

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[1] At Aussig 25,000 cells are required for 3,000 H.P.

The process was successfully worked at Niagara Falls between 1900 and 1907, when the works were destroyed by fire.

Evaporation and Concentration of the Caustic Soda and Potash.—The evaporation of the NaOH liquors, containing as they do much NaCl, is carried out in triple or quadruple effect vacuum pans very similar to those used in the manufacture of soap for evaporating the soap lyes and recovering the salt (see Martin's "Industrial Chemistry," Vol. I., "Organic").

In evaporation, advantage is taken of the fact that NaCl and KCl are very sparingly soluble in concentrated NaOH or KOH solution, and consequently, as soon as the concentration proceeds far enough, the NaCl separates out almost completely, and is separated from the NaOH liquors by forcing the whole through special filters. Thus (Fig. 20) A represents the body of the vacuum pan, the separating NaCl collects in B, which is provided with a transporting screw or worm, working automatically, which from time to time forces the deposited salt from B through the filter press C, wherein the salt remains behind while the NaOH liquors are sucked away into D, whence they are forced back again into A, and the evaporation continued until the right concentration is attained.

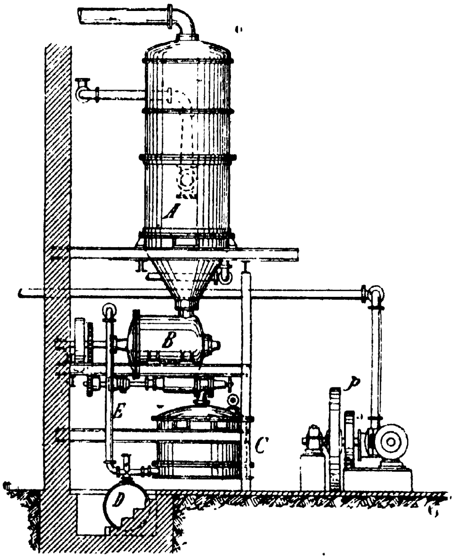

FIG. 20.—Vacuum Pan for Concentrating Caustic Soda.

The electrolytic NaOH of the Badische Anilin- und Soda-fabrik is used largely for the alizarin fusion. Large quantities of NaOH find an outlet in the paper, soap-making, and many other trades.

The electrolysis of KCl with the resulting production of KOH, Cl, and H is carried out in precisely the same manner as that of NaCl, and it is possible to obtain chlorine-free KOH by first evaporating to 50° Bé. (at which temperature the liquor contains 49 per cent. KOH to only 0.6 per cent. KCl,—so insoluble is KCl in concentrated KOH solution, the substance being often put on the market in this form), and after filtering the separated salt, by further concentration and crystallisation at 60° C., when the chlorine-free solid hydrate $KOH.H_2O$ is obtained. Below [illegible]° C. the hydrate $KOH.2H_2O$ is obtained.

The industry is especially developed in Germany, where in 1904 some 15,000 tons electrolytic NaOH and 28,000 tons electrolytic KOH were placed on the market, the evolved chlorine going to make some 60,000 tons of bleaching powder. In Germany two-thirds of the bleaching powder made is derived from electrolytic chlorine. In the U.S.A. the industry is also highly developed, but in the United Kingdom only a beginning has been made.

The chlorine which is evolved in these electrolytic processes is extremely concentrated, as much so as Weldon's chlorine. It is either directly converted into bleaching powder or liquefied.

The hydrogen, compressed in solid-drawn weldless steel cylinders to 150 atmospheres, is used for autogenous welding and cutting, for hydrogenating unsaturated organic substances, and for filling airships (see Martin's "Industrial Chemistry," Vol. II.). In Germany it is stated that 10,000,000 cubic metres are annually produced from this source alone.

Properties of Chlorine Gas.—Greenish-yellow, very irritant suffocating gas. Sp. gr. 2.5 (Air = 1). 1 vol. water absorbs of chlorine gas (measured at 0° C. and 760 mm.):—

Temperature	10° C.	20° C.	30° C.	90° C.
Vols. of chlorine	3.095	2.260	1.767	0.380

Sunlight decomposes chlorine water, causing evolution of oxygen:—

$$Cl_2 + H_2O = 2HCl + O.$$

Moist chlorine is very chemically active, uniting with H gas explosively in sunlight also with most metals (with exception of platinum), S, P, etc. Carbon is not attacked. Dry chlorine is much less active, having no action on sodium or even iron Chlorine is absorbed by sodium thiosulphate, caustic alkalies, lime, etc.

Powerful bleaching and oxidising agent in presence of moisture.

For **Liquid Chlorine**, see p. 31.

CHAPTER III

Liquid Chlorine

CHAPTER III

LIQUID CHLORINE

LITERATURE

See the foregoing references to chlorine on pp. 3, 13, also the following:—

TEICHMANN.—"Komprimierte Gase." 1908.

HOLBING.—"Fortschritte in der Fabrikation der anorganischen Sauren, der Alkalien, des Ammoniaks und verwandter Industriezweige, 1893-1905." Berlin, 1905.

O. KAUSCH.—*Zeit. comp. u. fluss. Gase*, 1893, **7**, 58.

Also German Patent, 50,329, 1888. American Patent, 491,699. English Patents, 13,[illegible]0, 1888; 7,058, 1890; 1889-1892.

Chem. Ind., 1906, **29**, 105; 1905, 698.

A. LANGE.—*Zeit. angew. Chem.*, 1900, 684, gives the physical properties of liquid chlorine.

GEOFFREY MARTIN and E. DANCASTER give a full account of the properties of gaseous and liquid chlorine in Vol. VIII. of "Modern Inorganic Chemistry." Edited by Newton Friend. 1915.

IN Germany, the production of large quantities of chlorine by electrolysis of alkali chloride solution has led to the manufacture of liquid chlorine on a considerable scale. Liquid chlorine is also made in England by the Kastner-Kellner Co. The industry arose from the observation of R. Knietsch (of the Badische Anilin- und Soda-fabrik), in 1888, that dry liquid chlorine does not attack iron. At the present time the liquid chlorine is sent long distances in large boilers mounted on wheels (somewhat similar to the apparatus used for transporting petroleum), and is drawn off from below in a liquid condition into storage vessels, from which it is allowed to issue from above as a gas when required for use.

When, however, only small quantities are required, the liquid chlorine is preserved in steel cylinders, holding from 80-120 lbs. or more of liquid chlorine.

By means of these methods chlorine has been rendered available in a convenient form, and is now generally used both on the large and small scale for chlorinating organic materials (*e.g.*, in the manufacture of **monochloracetic acid** for the preparation of indigo (see Martin's "Industrial Chemistry," Vol. I.), chloroform, chloral, carbon, tetrachloride, chlorbenzene, chlortoluene, etc.; also for obtaining bromine from bromides. Recently it has been employed in warfare.

Liquid chlorine is produced solely from concentrated electrolytic (or Weldon) chlorine. Diluted chlorine evolved from the Deacon process is quite unsuitable for liquefaction. The process is as follows:—

The concentrated chlorine as it streams from the electrolytic cells is cooled in earthenware pipes in order to condense as much water and hydrochloric acid (if any is present) as possible; the gas then passes through concentrated sulphuric acid in order to dry it, and then into the gas holder A, which stands over concentrated sulphuric acid (Fig. 21). From A the gas passes through the tube *bcd* into the compressing pump D.

The piston M works up and down in the limb P of the U-shaped tube RS. This U tube is filled with concentrated sulphuric acid, but the surface of the acid in P is covered with a layer of petroleum. The tube is widened at R in order to prevent the rise and fall of the liquid surface churning up the sulphuric acid and petroleum therein into an emulsion. The limb S communicates with the holder T by means of a valve N and a hole *l* (which can be wholly or partially closed by the screw *p*).

A water bath H surrounding S keeps the limb S at a temperature of 50°-80° C., so as to prevent chlorine condensing in this part of the apparatus. X is the strong glass tube to show the level of the liquid in T. The tube *g* leads to the condensing coil K and the strong steel holder O. The action is as follows:—When the plunger M rises in R the pressure is diminished, and Cl gas is sucked in from the tube *bcd* through the valve *f* into the chamber E. When, however, the plunger M descends on the return stroke, the chlorine which has entered is driven out of the chamber E through the valve N into T, the last traces of Cl being forced out of the chamber E into T by the excess of acid contained therein The complete expulsion of the Cl from the chamber above E is essential, because in order to liquefy chlorine gas it is necessary to compress it to about $\frac{1}{16}$ of its original value, so that if only a small bubble of chlorine remained in E this would greatly impair the efficiency of the pump. The hole *l* prevents this, for as soon as the pressure decreases in E

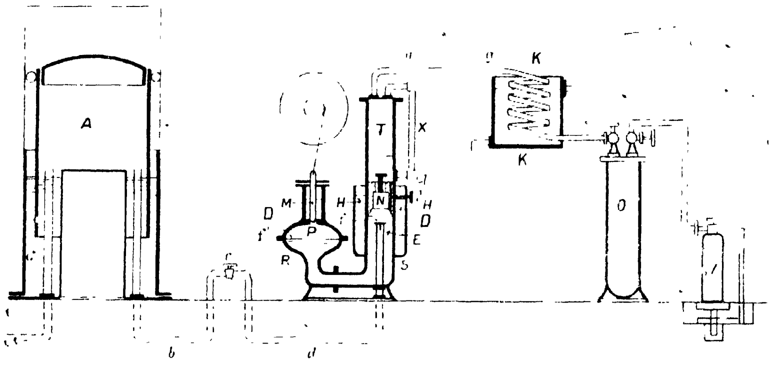

FIG. 21 —Plant for Liquefying Chlorine.

(owing to the rise of the plunger M) a quantity of acid is sucked from T through the tube *l* into this chamber E so as to partially fill it, and consequently somewhat less Cl is sucked into the chamber E from *f* than properly corresponds to the volume of the plunger M of the pump When now the plunger M returns on its downward stroke, it follows that not only is all the Cl pressed out of E into T, but also the excess of sulphuric acid which had entered the chamber E through *l* is also expelled, and this stream of acid forces out the last traces of Cl from E into T.

The compressed chlorine passes away from the pump through *g* into the condensing coil K. Here liquefaction takes place, the liquid pouring into the strong steel vessel O, and then into the steel cylinder V, which stands upon a weighing machine. The steel transport cylinders are made of such a size that they will hold, say, 50 kg. (about 1 cwt.) of chlorine. It should be noted that for each 1 l. capacity not more than 1.25 kg. of liquid chlorine can be run in, or 1 kg. of chlorine must have allowed it 0.8 l. (The specific gravity of liquid chlorine at – 10° C. is about 1.5.) 1 kg. Cl corresponds to about 300 l. of Cl. These cylinders are usually tested every two years up to 22 atmospheres pressure.

The firm, P. Schültze & Co., have placed on the market a double-action compressor for chlorine and similar very reactive gases, a section of which is shown in Fig. 22. The apparatus is worked by compressed air. The whole apparatus is made of acid-resisting cast iron The compressing pistons for the chlorine are formed by liquid sulphuric acid of 60° Bé. contained in the two vessels V, V.

The sulphuric acid in these two vessels alternately rises and falls, being operated by compressed air entering through A. When the liquid in V falls, it sucks in chlorine gas through the valve H; and when it rises it expels the chlorine gas in a compressed condition (about 8 atmospheres) through the valve F. A glass tube (shown in outline) indicates clearly what is taking place in each of the vessels V. The chlorine gas, therefore, only comes into contact with the sulphuric acid in V, and the walls of V (which are often porcelain or lead-lined cast iron). By this means all difficulties as regards pistons, stuffing boxes, etc., are avoided. The way that the compressed air entering through A causes the sulphuric acid in D and the chambers V, V to alternately rise and fall is as follows:— The compressed air rushing in through A into the chamber D forces the sulphuric acid out of D into V, thereby compressing the chlorine in V and expelling it through F. When, however, the sulphuric acid is nearly expelled from D the floater B is left without support, and immediately sinking operates

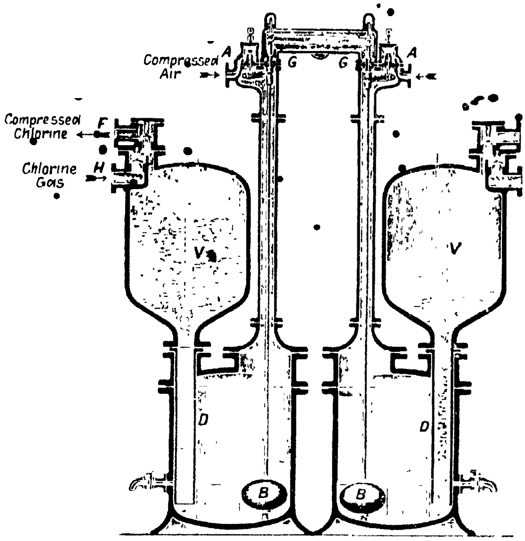

FIG. 22.—Double Action Compressor for Liquefaction of Chlorine.

a lever which shuts off the supply of compressed air, and simultaneously opens the valve G, thus allowing the compressed air in D to escape into the air. The pressure thus falls in D, which causes the sulphuric acid in V to rush back again into D, thus again drawing in fresh chlorine through H. The mechanism is so arranged that when the sulphuric acid in one chamber V is rising, the sulphuric acid in the other chamber V is falling.

Liquid chlorine is a yellow mobile liquid, boiling at −34° C. At 15° C. it has a vapour pressure of 5.8 atmospheres, and consequently it can be easily liquefied either by compressing to 8 atmospheres and cooling with water, or by cooling to −50° C. by means of liquid CO_2.

The specific gravity of liquid Cl is 1.5950 at −50°, 1.4685 at 0° C., 1.4257 at 15° C., 1.3141 at 50° C., 1.2228 at 75° C., and 1.1134 at 100° C.

For properties of **Chlorine Gas** see p. 25.

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CHAPTER IV

Manufacture of Chlorates and Perchlorates

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MANUFACTURE OF CHLORATES AND PERCHLORATES

LITERATURE

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Manufacture of Sodium and Potassium Chlorate.—Potassium chlorate, $KClO_3$, and sodium chlorate, $NaClO_3$, form excellent oxidising agents, containing the chlorine absorbed in their formation available for oxidising purposes ($6Cl = 3O$), hence chlorates are much used for oxidising purposes in various technical processes, in the preparation of dyes, and in cloth printing: also large quantities of chlorate are used in the manufacture of explosives and matches. The chief difference between sodium and potassium chlorates is the fact that potassium chlorate is only sparingly soluble in cold water, but readily soluble in hot, so that it is easy to obtain this substance in a finely crystalline and pure condition. Sodium chlorate, however, is easily soluble in cold water as well as in hot, and so in cold aqueous solution is somewhat easier to use than potassium chlorate, but more difficult to manufacture.

Two processes of manufacture are in use. According to the old process chlorine gas is led into hot milk of lime, and the difficultly crystallisable calcium chlorate thus produced is converted into potassium or sodium chlorate by adding excess of KCl (or NaCl).

The more recent electrolytic process is being largely worked in the United States (Niagara Falls), Sweden, and the Alps, where cheap hydro-electric power is available. However, the old process at the time of writing is holding its own against these newer processes. We will describe each process in turn.

Old Process for Manufacture of Chlorates.—Milk of lime is placed in a large iron cylinder provided with a stirring apparatus, and a stream of chlorine is led into the liquid. Heat is evolved, and the liquid spontaneously increases its temperature to 40°-50° C., when the calcium hypochlorite at first formed is almost entirely decomposed into chlorate, according to the equations :—

$$(1)\ 2Cl_2 + 2Ca(OH)_2 = \underset{\text{Calcium hypochlorite.}}{Ca(OCl)_2} + \underset{\text{Calcium chloride.}}{CaCl_2} + 2H_2O.$$

$$(2)\ 3Ca(OCl)_2 = \underset{\text{Calcium chlorate.}}{Ca(ClO_3)_2} + \underset{\text{Calcium chloride.}}{2CaCl_2}.$$

Or, expressed in one equation :—

$$6Cl_2 + 6Ca(OH)_2 = Ca(ClO_3)_2 + 5CaCl_2 + 6H_2O.$$

Towards the end of the reaction a pink colour appears in the liquid, due to the formation of small quantities of permanganate, owing to the presence of traces of manganese in the lime. The liquid is now neutralised and filtered, and then excess of KCl is added, when potassium chlorate is formed and crystallises out :—

$$2KCl + Ca(ClO_3)_2 = 2KClO_3 + CaCl_2.$$

On cooling the mother liquors strongly with special refrigerating machines a further crop of $KClO_3$ separates. The mother liquors are very rich in $CaCl_2$, the technical utilisation of which (as in the Weldon and Ammonia-Soda processes) is one of the unsolved problems of chemical industry (see Martin's "Industrial Chemistry," Vol. II.).

The potassium chlorate is freed from chloride by recrystallisation. The preparation of **sodium chlorate** differs from that of potassium chlorate, owing to the fact that it is much more easily soluble in cold water, and thus more difficult to separate by crystallisation. 100 parts of cold water at 20° C. dissolve 7.3 parts of $KClO_3$ against 99 parts of $NaClO_3$. Hence in this case the procedure is as follows.—To the neutralised and filtered calcium chlorate solution excess of NaCl solution is added, and the liquor allowed to evaporate until calcium chloride, $CaCl_2$, separates out in a crystalline state. Now Glauber salt (sodium sulphate) is added so as to precipitate the rest of the calcium salts in solution as calcium sulphate :—

$$CaCl_2 + Na_2SO_4 = CaSO_4 + 2NaCl;\ Ca(ClO_3)_2 + Na_2SO_4 = CaSO_4 + 2NaClO_3.$$

The sodium chloride and sodium chlorate in the mother liquors are then separated by crystallisation, sodium chloride being much less soluble in water than sodium chlorate.

In practice it is found that about seven times more chlorine is necessary to produce 1 part of potassium chlorate than the same weight of bleaching powder. From the preceding equations it will be seen that, theoretically, some five-sixths of the chlorine used passes away as the almost worthless $CaCl_2$ (practically considerably more than five sixths of the used chlorine is wasted), but the chlorine thus absorbed is converted into the equivalent amount of available oxygen in the resulting chlorate. This is seen from the equations :—

$$12Cl = 6O.$$
$$12Cl + 6Ca(OH)_2 = Ca(ClO_3)_2 + 5CaCl_2 + 6H_2O.$$
$$Ca(ClO_3)_2 = CaCl_2 + 6O.$$

Manufacture of Chlorates and Perchlorates by Electrolysis.—When an electric current is passed through a hot aqueous solution of potassium chloride, KCl, the current, under certain conditions, can split up the water, oxygen being evolved at the + pole (anode) and hydrogen at the − pole ($H_2O = H_2 + O$). The KCl also undergoes decomposition, KOH and hydrogen being produced at the − pole and Cl at the positive pole ($KCl = K + Cl$; $K + H_2O = KOH + H$). If, however, these different products are not automatically separated as formed, but are liberated under such conditions that they can all react together at a temperature of 45°-100° C., we get the chlorine absorbed by the KOH formed, forming hypochlorite ($2KOH + 2Cl = KClO + KCl + H_2O$), and the nascent oxygen also absorbed in oxidising the hypochlorite to chlorate ($KClO + 2O = KClO_3$). Also the hypochlorite spontaneously decomposes into chlorate ($3KOCl = KClO_3 + 2KCl$). It is thus possible, by carrying out the electrolysis of KCl solution under suitable conditions, to obtain an excellent yield of $KClO_3$, the final result being expressible by the equation :—

$$KCl + 3H_2O = KClO_3 + 3H_2.$$

Practically only traces of free oxygen or chlorine are evolved.

Gall and Montlaux (Switzerland) were the first (1889-1890) to successfully produce chlorates on the large scale by electrolytic processes, and so long ago as 1900 their factories at Vallorbe and S. Michel were producing some 3,000-3,500 tons of chlorate annually.

The first cells of this firm were provided with diaphragms and the alkaline cathodic liquors were transferred to the anodic compartment by special means. At the present time, however, the use of diaphragms has been given up, and the neutral KCl solution is simply electrolysed, using platinum-iridium net anodes with stirrers in the cell to bring the chlorine into contact with the KOH produced at the cathode.

The bath is heated by the passage of the current to over 40° C. The bath liquors, when containing sufficient $KClO_3$, are removed, the $KClO_3$ allowed to crystallise out, and the mother liquors, again saturated with KCl, are allowed to run back into the electrolyser.

In **Gibb's Process**, as used at the National Electrolytic Co., at Niagara Falls, N.Y., the cell consists of a wooden trough lined with lead and divided into a number of compartments. Fig. 23 shows a longitudinal section through the cell The anodic surfaces B are sheet-lead covered over with platinum foil. The cathodes consist simply of a number of copper wires C, fixed vertically in the cell by insulating bars O. F,F are insulating strips. A continuous stream of alkali chloride solution is led in through G to the bottom of the apparatus, and the chlorate produced in the cell, together with unchanged KCl and H gas, escapes through the openings H.

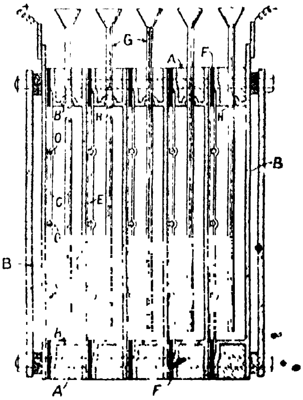

FIG. 23.—Gibb's Electrolytic Cell for Chlorate.

The temperature of the bath is kept at 60°-70° C., when the brine flows through the cells at the rate of 28 l per hour, while the yield from the current is about 70 per cent. of theory. The current density employed amounts to 55 amperes per square metre at the anode, the current going through the series of cells being 1,650 amperes. The works at Niagara use 2,000 H.P. from the falls. The escaping liquors must not contain more than 30 per cent. chlorate per litre.

In **Lederlin and Corbin's Cell** (see French Patents, 226,257 of 1892, and 238,612, of 1894) a large number of platinum foil electrodes C (Fig. 24), fixed close together in ebonite holders B in a tank of cement, are employed. The hot current of alkali chloride solution, entering at O, flows between these electrodes C, and so is converted into chlorate in the usual way. The solution of chlorates run off at Q. G and H are wooden supports for the ebonite holders. This apparatus has been successfully employed on the large scale, and has been working since 1895 in a number of Continental factories.

Since the formation of potassium chlorate takes place according to the equation :—

$$KCl + 3H_2O = KClO_3 + 3H_2$$

(only very little oxygen being evolved through secondary decomposition of water), about ½ cub. m. of hydrogen gas is evolved to every 1 kg. $KClO_3$ produced.

Considerable losses of current ensue by the reduction of the hypochlorite formed at first by the hydrogen evolved at the cathode, and many proposals have been made to overcome this difficulty. Thus the addition of 0.2 per cent. $CaCl_2$ (see French Patent, 283,737 ; German Patent, 159,747, of 31st May 1904) or the presence of potassium dichromate and HCl (see German Patents, 110,505, is led into the liquid. Heat is evolved, and the liquid spontaneously increases its temperature to 40°-50° C., when the calcium hypochlorite at first formed is almost entirely decomposed into chlorate, according to the equations:—

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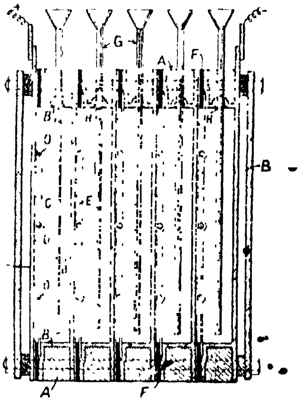

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The slight evolution of chlorine at the beginning of the electrolysis may be avoided by adding KOH to the bath, a process, however, which diminishes the yield from the current employed. Better yields are obtained by keeping the electrolyte slightly acid, when the free hypochlorous acid formed promotes the formation of chlorate according to the equation:—

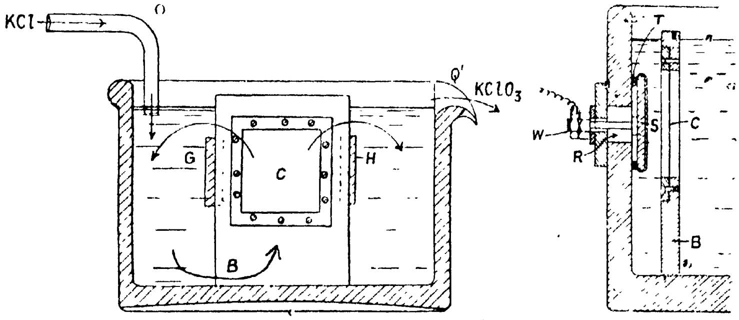
$$KOCl + 2HOCl = KClO_3 + 2HCl.$$

The current needed for producing one gram-molecule (122.5 g.)—

$$KClO_3 = 6Cl = \frac{96540 \times 6}{60 \times 60} = 161 \text{ amperes per hour.}$$

A current of 1 ampere in twenty-four hours can yield 18.3 g. $KClO_3$.

The manufacture of sodium chlorate, $NaClO_3$, from salt ($NaCl$) is carried out just as the manufacture of $KClO_3$ from KCl, but owing to the great solubility of $NaClO_3$ in water a complete separation of the $NaClO_3$ from the NaCl is only attained by repeated recrystallisation.



Section through the Cell.

Section through Electrode.

FIG. 24.—Lederlin Corbin Electrolytic Cell for Chlorate.

Manufacture of Perchlorates.—When the percentage of sodium chloride in the electrolytic bath falls below 5 per cent. perchlorate, $NaClO_4$ is formed, together with chlorate, $NaClO_3$:

$$NaCl + 4H_2O = NaClO_4 + 4H_2,$$
$$NaCl + 3H_2O = NaClO_3 + 3H_2.$$

If the temperature is kept low and the current density small all the chlorate will disappear, being converted into perchlorate—

$$NaClO_3 + H_2O = NaClO_4 + H_2.$$

With 10 per cent. NaCl or more in solution perchlorate is not formed in noticeable quantities, and also perchlorate is not formed in hot baths. The conditions of formation of perchlorate from chlorides, therefore, are dilute solutions of chloride, low temperatures, and low current densities. However, in the manufacture of perchlorates, usually they are not obtained directly from chloride solutions, but the chloride is converted first into chlorate, and then the chlorate so obtained is electrolysed into perchlorate.

Winteler (*Chemiker Zeit.*, 1898, 89) has worked out in detail the best conditions. Assuming that the solution only contains chlorates, he finds that these conditions are:—(1) A low temperature at anode, (2) an acid solution at anode, (3) current density, 8-12 amperes per square metre, (4) high concentration of the electrolyte, (5) artificial cooling of the electrodes.

Lederlin (German Patent, 136,678, of 1901) adds bichromate to the electrolyte (best by adding chromate and then at periodic intervals running in some free HCl). He claims that this procedure greatly increases the yield of perchlorate. Wilson (German Patent, 143,347, of 1902) advises the presence of a little free chlorine in the bath.

Couleru (*Chem. Zeit.*, 1906, 30, 213) states that the electrolysis of the NaCl solution is continued until a solution containing some 750 g. per litre of sodium chlorate, $NaClO_3$, is obtained—thereby saving the expense of concentrating the liquid. A crude sodium chlorate is deposited from this solution, which is then redissolved in water, and so a solution containing practically only chlorate is obtained, the presence of chloride or hypochlorite being injurious. This chlorate solution is then electrolysed for perchlorate, using platinum anodes and iron cathodes, the electrolysis being carried out in as concentrated a solution of chlorate as possible.

Any alkali formed is neutralised, and the bath is kept between 8° and 10° C., a temperature over 25° C. being very injurious indeed. The temperature is kept low either by means of cooling coils inserted in the bath, or else the electrodes are themselves cooled internally, special refrigerating machines being used for the purpose.

The current density, and also the addition of various substances to the electrolyte, does not effect to any great degree the yield, which amounts to 85 per cent. of theoretical. The electrolysis should be continued until all the chlorate is converted into sodium perchlorate, which, being very soluble in water, does not crystallise out. Sodium perchlorate, moreover, is hygroscopic, and so is quite unsuitable for the manufacture of explosives and fireworks. It is therefore never isolated as such, but is always directly converted into the more convenient and non-hygroscopic **potassium perchlorate**, $KClO_4$, or **ammonium perchlorate**, NH_4ClO_4, by adding to the content sodium perchlorate solution excess of KCl or ammonium salts (NH_4Cl or NH_4NO_3), and crystallising out.

$KClO_4$ is only sparingly soluble in cold water, 1,000 c.c. cold water merely taking up 15 g. $KClO_4$, and hot water some 180-225 g., so that it is very easily separated by crystallisation from NaCl, which is much more soluble in cold water. 1,000 c.c. cold water dissolves 250 g. ammonium perchlorate, and so the ammonium perchlorate is somewhat more difficult to free from NaCl by crystallisation; however, as the solubility of the ammonium salt rapidly increases with the temperature, in practice not much difficulty is experienced in preparing pure ammonium perchlorate.

The crude salts which crystallise out are washed with a little water, and are obtained easily 99 per cent. pure. They are dried with steam, or hot air, at a temperature below 100° C.

In a wet state the substances are not in any way dangerous; when dry, however, and mixed with oxidisable organic matter, they may set up dangerous explosive combustion, and accidents have occurred owing to workmen's clothing becoming impregnated with the liquors, which have then dried.

Considerable amounts of perchlorates are manufactured for explosives, perchlorates being better adapted for this purpose than chlorates, both on account of their greater stability and their higher percentage of oxygen.

Analysis.—The amount of perchloric acid is not estimable by titration, as the contained oxygen is not active. The amount of metal in the salt is, therefore, obtained in the usual gravimetric manner, and so the amount of perchlorate is calculated from this.

CHAPTER V

Bleaching Powder and Hypochlorites

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CHAPTER V

BLEACHING POWDER AND HYPOCHLORITES

LITERATURE

LUNGE.—"Sulphuric Acid and Alkali." 1913.
ENGELHARDT.—"Hypochlorite und Elektrische Bleiche" 1903

BLEACHING POWDER

WHEN moderately dry[1] slaked lime is treated with chlorine in the cold, it absorbs some 35-36 per cent. of chlorine to form a dry white powder, which possesses strong bleaching and disinfecting properties, and is known as "bleaching powder" or "chloride of lime." These properties arise from its power of giving off the absorbed chlorine again when treated with acids. Although commercial bleaching powder usually contains only 35-36 per cent. "available" chlorine, yet, if the temperature of the lime be kept between 30° C. and 40° C., a bleaching powder containing some 40 per cent of available chlorine may be obtained. Under very special circumstances lime has been known to take up as much as 43.5 per cent. of "available" chlorine. The actual amount of available chlorine in bleaching powder depends greatly on the mode of manufacture, its age, etc.

The following are typical analyses of good bleaching powder:—

	Per Cent.		Per Cent.
Available chlorine	36-38.3	*Alumina*	0.3-0.4
Chlorine as chloride	0.32-0.60	*Manganese oxide*	trace
Chlorine as chlorate	0.08-0.26	*Carbonic acid*	0.2-0.5
Lime	43.5-44.5	*Silica*	0.3-0.5
Magnesia	0.3-0.4	*Water and loss*	16.3-17.0
Ferric oxide	0.02-0.05		

Lunge and Schappe made a bleaching powder with perfectly pure lime so as to obtain the greatest absorption possible of chlorine. The sample contained:—

	Per Cent.
Available chlorine	43.13
Chlorine as chloride	0.29
Lime	39.89
CO_2	0.42
H_2O (direct estimation)	17.00
	100.73

In 1785 C. L. Berthollet, in Paris, discovered the bleaching action of "Javel water," produced by the action of chlorine on potash. Watt brought the news to Glasgow, and in 1798 Charles Tennant patented a process for use of cheaper lime instead of potash, this patent being subsequently declared void because lime had been used for the same purpose in Lancashire for some years prior to Tennant's patent. It was therefore only natural that the action of the chlorine in the

---

[1] Perfectly dry slaked lime, $Ca(OH)_2$, is not acted on at all by chlorine. For the best results the lime should contain some 4 per cent. of excess water over that required for the formula $Ca(OH)_2$, and the lime should be as pure as possible.

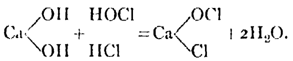
$Ca(OH)_2$ was thought to be similar in nature to that which occurs when chlorine is led into cold KOH or NaOH solutions, when potassium or sodium hypochlorites (KClO or NaClO) are formed, and so bleaching powder was at first thought to be merely a mixture of $CaCl_2$ and calcium hypochlorite, $Ca(ClO)_2$, produced thus:—

$$2Ca(OH)_2 + 2Cl_2 = \underset{\text{Calcium hypochlorite.}}{Ca(ClO)_2} + \underset{\text{Calcium chloride.}}{CaCl_2} + 2H_2O.$$

However, it seems practically certain that **ordinary dry** bleaching powder does not contain calcium hypochlorite, $Ca(ClO)_2$, as such, and the exact constitution of dry bleaching powder or "chloride of lime" is still a matter of dispute. Balard gave it the formula $Ca(OCl)_2.CaCl_2 + Ca(OH)_2$; while Stahlschmidt proposed the formula $Ca(OCl)(OH).CaCl_2.2H_2O$. However, the formula now most favourably received is that suggested in 1861 by W. Odling, who assumed that the essential component of bleaching powder was the compound Cl—Ca—OCl, which is mixed with uncombined lime, $Ca(OH)_2$.

Commercial bleaching powder is best represented by such a formula as $Ca(OCl)Cl + n.Ca(OH)_2$, where n = nearly $\frac{1}{2}$, that is to say, $2Ca(OCl)Cl + Ca(OH)$.

The formation of the compound Cl—Ca—OCl could be regarded as due to the neutralisation of lime by a molecule of each of the monobasic acids formed by the action of chlorine on moisture present in the lime, thus:—



$$Ca\begin{matrix}\diagup OH \\ \diagdown OH\end{matrix} + \begin{matrix}HOCl \\ HCl\end{matrix} = Ca\begin{matrix}\diagup OCl \\ \diagdown Cl\end{matrix} + 2H_2O.$$

It is very probable that Odling's formula is correct, and that dry bleaching powder does not contain any calcium chloride as represented by Balard's and Stahlschmidt's formulæ, for the following reasons:—(1) The chlorine can be completely expelled from bleaching powder by moist CO_2 at 70° C., whereas $CaCl_2$ is not so decomposible. (2) Good bleaching powder is not deliquescent, as it would be if $CaCl_2$ as such was present in it; also $CaCl_2$ is readily soluble in alcohol, whereas alcohol extracts very little $CaCl_2$ from bleaching powder. (3) Bleaching powder cannot be made to take up more than 43.5 per cent. of Cl.

Although ordinary bleaching powder is regarded as not containing calcium hypochlorite, $Ca(OCl)_2$, as such, but rather the compound Cl-Ca-O-Cl, yet this only applies to *dry* bleaching powder. As soon as the bleaching powder is thrown into excess of cold water it is decomposed thus:—

$$\underset{\text{Bleaching powder}}{2Ca(OCl)Cl} = \underset{\text{Calcium hypochlorite.}}{Ca(OCl)_2} + \underset{\text{Calcium chloride.}}{CaCl_2}.$$

The calcium hypochlorite, $Ca(ClO)_2$, and calcium chloride pass into solution, whilst the unchanged calcium hydroxide forms an insoluble layer at the bottom, the solution possessing an intensely alkaline reaction owing to the presence of some dissolved $Ca(OH)_2$, which, of course, is a strong base. It has been suggested that hydrolysis takes place, thus:—

$$Ca(OCl)_2 + H_2O = Ca(OH)_2 + HOCl.$$

The practical application of bleaching powder depends upon the fact that when excess of acid is added to the solution, practically all the chlorine is evolvable as free chlorine, thus:—

$$Ca(ClO)_2 + CaCl_2 + H_2SO_4 = 2CaSO_4 + 2H_2O + 4Cl.$$
$$Ca(ClO)_2 + CaCl_2 + 2HCl = 2CaCl_2 + 2H_2O + 4Cl.$$

It is probable that the liberation of chlorine by acids is due first to the formation of hypochlorous acid, HOCl, thus:—

$$Ca(OCl)Cl + HCl = HOCl + CaCl_2.$$

The hypochlorous acid formed is very unstable and decomposes with excess of acid liberating chlorine, thus:—

$$HOCl + HCl = Cl_2 + H_2O.$$

Very dilute acid added to bleaching powder liberates hypochlorous acid, HOCl, alone.

It is the amount of chlorine thus set free, the "available chlorine" as it is called, which determines the technical value for bleaching purposes.

In bleaching with bleaching powder or with sodium or potassium hypochlorite, the fabric is steeped in a dilute aqueous solution of the bleaching agent, and then in dilute acid. Hypochlorous acid, HClO, is liberated as above described, and then free chlorine. The chlorine acts on the moisture of the wet fibre, liberating nascent oxygen ($H_2O + Cl_2 = 2HCl + O$) which oxidises the colouring matter of the fibre into a colourless oxidation product, and so "bleaches" the fibre.

Treating with acid in this manner causes a rapid and energetic bleaching action to take place. However, treating the fabric with a dilute aqueous solution of bleaching powder causes a moderate and even bleaching action, which is accelerated by the action of atmospheric CO_2.

The bleaching action of hypochlorous acid is generally stated to be twice that of the chlorine it contains, supposing that this latter were to be in a free state, as may be seen from the two equations:—

$$Cl_2 + H_2O = 2HCl + O; \quad 2HOCl = 2HCl + 2O.$$

However, as seen from the equation representing the manufacture of bleaching powder or hypochlorites (*e.g.*, $2Ca(OH)_2 + 4Cl = Ca(ClO)_2 + CaCl_2 + 2H_2O$, $2KOH + 2Cl = KOCl + KCl + H_2O$), since two atoms of chlorine are required to form one molecule of HOCl (since an equivalent of HCl is formed at the same time), this advantage appears practically to be somewhat illusionary.

Manufacture of Bleaching Powder.—For the manufacture of good quality bleaching powder the lime must be carefully slaked so as to form a dry powder, containing about 4 per cent. more water than corresponds to the formula $Ca(OH)_2$. Perfect dry lime does not absorb chlorine at all. The lime should be as pure as possible, and is passed through a sieve before use. The chlorine gas should be cool and dry, and carefully freed from HCl; it should not contain much CO_2. The presence of a little CO_2 in electrolytic or Weldon chlorine (which is very concentrated) does not matter, because CO_2 acts on the $Ca(OH)_2$ much more slowly than the chlorine. Generally speaking, 64 parts of slaked lime yield 100 parts of 36 per cent. bleaching powder.

For the manufacture of bleaching powder two kinds of technical chlorine are available—(1) The very concentrated Weldon or electrolytic chlorine, which acts rapidly and energetically on the lime. (2) The very dilute Deacon's chlorine, which acts less energetically. Entirely different plants are used with these two kinds for chlorine, and we will describe each separately.

1. **Manufacture of Bleaching Powder from Concentrated Weldon or Electrolytic Chlorine.**—The lime is spread in 3 or 4 in. layers on the floor of a large "chlorine chamber," some 6 or 7 ft. high, 10-20 ft. wide, and 100 ft. long. The walls are made out of tarred or asphalted sandstone slabs (asphalt being very resistant towards chlorine); in modern practice, however, the top and sides are made of sheet lead fastened by straps on timber work, like vitriol chambers. The entrance is covered over with asphalted iron plates. The layer of chlorine is raked into furrows in order to expose a larger surface, and a stream of chlorine is led into the chamber from one of the ends of the chamber; an opening in the other end of the chamber allows the air to escape. Two windows allow the interior to be viewed and the flow of chlorine to be turned off as soon as the chamber is full. The outlet is also closed when the chamber is filled with chlorine. The chlorine enters through a pipe placed at one end near the roof of the chamber; being a heavy gas it sinks downwards, and is at first rapidly absorbed by the lime; later the absorption becomes slow and the temperature rises, but great care must be taken that this latter never exceeds 25° C. Great excess of chlorine should also be avoided, and so usually a definite amount of chlorine is let into the chamber; the chamber is closed and allowed to stand some twelve to twenty-four hours. In order to expose a fresh surface the lime is turned over from time to time. Finally, before allowing workmen to enter the chamber and remove the bleaching powder, the last residues of chlorine must be sucked out, either by passing in a stream of air, or simply by injecting some finely powdered lime dust (English Patent, 7,199, 1886; *cf.* "Twenty-third Report on Alkali, etc., Works," 58-60), which absorbs most of the chlorine.

A chamber making 10 tons of bleaching powder and containing fair excess of chlorine requires some 4-5 cwt. of lime dust blown in through a special fan or distributor. This reduces the Cl in the chambers to about 0.8 gr. per cubic foot, producing 6 cwt. of extra bleaching powder, and requiring about two hours to settle. Before allowing workmen to enter, the air of the chambers (which should be tested by the works' chemist) should not contain more than $2\frac{1}{2}$ gr. of Cl per cubic foot. Bleaching powder chambers should have about 200 sq. ft. of chamber space per ton of bleaching powder made per week (see "Twenty-first Report on Alkali, etc., Works," p. 12, for rules).

The bleaching powder is then packed into very well-made wooden casks (but of hard wood) for transport and storage.

The ends are coated with plaster of Paris to prevent access of air, which soon spoils the powder; the full casks must be stored in a cool, dry place, both rain and sunshine damaging the material.

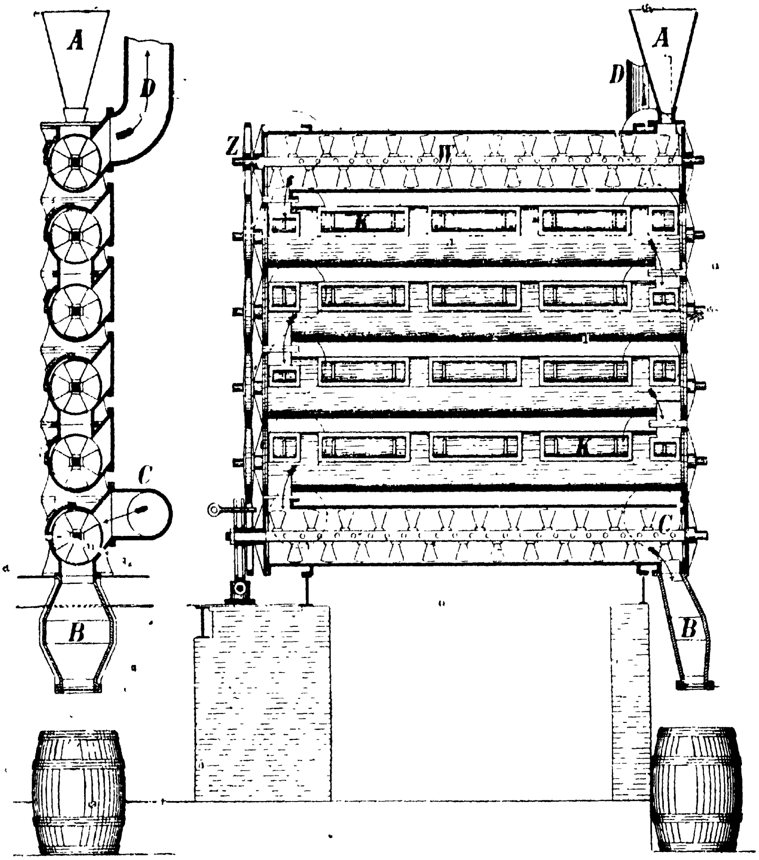


FIG. 25.—Hasenclever's Cylinder Apparatus for Bleaching Powder.

The *yield* of bleaching powder is usually $1\frac{1}{2}$ times the weight of the slaked lime.

Since the raking over and indeed entry of the chlorine chambers by workmen is very injurious for the health, and has often been attended by fatal accidents, many devices have been proposed and adopted for minimising the risks. In some forms of apparatus the lime is laid on perforated shelves of the chlorine chambers, and the raking of the half-finished bleaching powder is entirely worked from outside by mechanical appliances. These plants do not seem, however, to have been very successful.

2. Manufacture of Bleaching Powder from Dilute Deacon Chlorine.—The diluted chlorine evolved from the Deacon process is not suitable for making a good bleaching powder from the chamber process above described, and so an entirely different sort of apparatus is usually employed, being known, from the name of its inventor, as "Hasenclever's Cylinder Apparatus" (English Patent, 17,012, 1888). It is illustrated in Fig. 25.

The apparatus consists of six or eight cast-iron cylinders, lying vertically one above the other, of length some 12-20 ft., each provided with a feeding worm W, which is kept revolving slowly by means of the cog-wheels Z. The slaked lime is poured in at A into the topmost cylinder, and is gradually moved downwards, as indicated by the arrows, from cylinder to cylinder until it finally escapes from the bottom cylinder at B. Meanwhile the Deacon chlorine, freed as much as possible from HCl and CO_2, is passed at C into the bottom cylinder, and streams along in a direction opposite to that of the moving slaked lime, finally escaping at the topmost cylinder by the pipe D. The chlorine is all absorbed by the lime, and there escapes at D a practically chlorine-free gas. The bleaching powder is let out from B from time to time into a wooden cask situated below. Since chlorine gas might attack the iron work of the spur wheels, the latter are painted with $BaSO_4$ (Blanc fixe). Each of the cylinders is provided with a number of lids K,K, which can be removed when the apparatus becomes blocked up, or when some other disturbance necessitates the interior of the cylinders being investigated.

By this apparatus no danger results to the workmen (as in the chamber process), because they do not come into contact either with the lime dust or with the chlorine fumes. The resulting bleaching powder contains about 36 per cent. of available chlorine.

The apparatus cannot be used for the production of bleaching powder from concentrated chlorine, such as comes from the Weldon or electrolytic processes, because the lime would heat up too quickly.

Deacon's Apparatus consists of chambers provided with large numbers of shelves; the lime is spread in 1-in. layers on these shelves, and the chlorine allowed to circulate over them in such a manner that the strongest Cl comes into contact with nearly finished bleaching powder, and the last gas, containing only traces of Cl, is passed into fresh lime.

Manufacture of Pure Calcium Hypochlorite.—Pure calcium hypochlorite, $Ca(ClO)_2$, has recently been manufactured by the Griesheim-Elektron Company (German Patent, 188,524, of 27th April 1906) by slowly passing chlorine gas into a cold aqueous milk of lime, filtering the liquid, and evaporating the still alkaline liquid in vacuum when colourless crystals of $Ca(ClO)_2$ separate. These are washed and dried *in vacuo* when a dry white powder, free from moisture and water of crystallisation, is obtained in which no less than 80-90 per cent. of the chlorine present is in the form of available chlorine. It is claimed that this kind of bleaching powder is more stable and keeps better than that obtained by usual methods. The crystals, if not rapidly deprived of water, lose much chlorine.

According to another patent taken out by the same firm (German Patent, 195,896, of 10th March 1907) if the chlorination be carried out with a concentrated solution of slaked lime, so that the specific gravity of the filtered solution exceeds 1.15, then we get precipitates of double compounds of lime and calcium hypochlorite, of composition $Ca(OCl)_2.2Ca(OH)_2$ and $Ca(ClO)_2.4Ca(OH)_2$. These insoluble substances require a considerable volume of water to split them up and withhold from effective use a considerable amount of available chlorine, causing much of the milkiness in the ordinary solutions of bleaching powders. However, if the passage of chlorine into the liquid is continued these compounds are gradually attacked, the $Ca(OH)_2$ taking up chlorine and being converted into $Ca(ClO)_2$. Hence, in order to prepare very strong solutions, we must first of all add to a chlorinated slaked lime solution a weighed quantity of slaked lime, when a precipitate occurs of the above compounds; then chlorine gas is passed in until the precipitates are dissolved again by the complete chlorination of the lime. By repeating the addition of lime and leading in chlorine again, it is possible to obtain calcium hypochlorite solutions of almost any strength until the pure $Ca(OCl)_2$ crystals begin to separate. The presence of $CaCl_2$ solutions favours the crystallisation.

Valuation of Bleaching Powder.—For typical analyses of bleaching powder see p. 43. Bleaching powder is a very unstable substance. It is decomposed by atmospheric moisture, the carbon dioxide of the air acting as a feeble acid as above indicated (p. 44). It even decomposes slowly when kept in a well-stoppered bottle. The loss of available chlorine on storage in a cool, dark place (where it is at a minimum) amounts to ¼ per cent. to ½ per cent. per month. In sunlight the loss is much more rapid than this, and is attended with the evolution of oxygen. The solution is much more unstable than the dry solid, decomposing on warming in two different directions, as represented by the two equations:—

$$3Ca(ClO)_2 = Ca(ClO_3)_2 + 2CaCl_2 ; \; Ca(ClO)_2 = CaCl_2 + 2O.$$

It is, of course, very important to determine the amount of "available" chlorine present in a sample of bleaching powder.

This is done as follows:—

A weighed quantity of bleaching powder is thoroughly ground with water and made up to a measured volume by dilution with water. This solution is then titrated by adding excess of Ki solution. On adding acetic acid, chlorine is liberated from the bleaching powder, which sets free its equivalent of iodine ($Cl_2 + 2Ki = 2KCl + I_2$), which latter is then titrated in the usual way with starch and sodium thiosulphate. 1,000 c.c. of $\frac{N}{1}$ sodium thiosulphate used up correspond to 35.5 g. of available chlorine present.

Another method is to titrate the bleaching powder solution with decinormal sodium arsenite solution, the end of the reaction being determined by means of starch, and KI used as an outside indicator. When the titration is complete a drop of the liquid, removed and placed on paper impregnated with starch and KI, will no longer give a blue stain. The amount of sodium arsenite solution used up is related to the amount of bleaching powder by the following equation:—

$$Ca(OCl)Cl + Na_3AsO_4 = Na_3AsO_4 + CaCl_2.$$

In other words, 1,000 c.c. of $\frac{N}{1}$ sodium arsenite solution used up correspond to 35.5 g. of available chlorine.

In some works, especially in Germany, bleaching liquids are obtained on the spot as required, by passing chlorine gas (evolved from liquid chlorine in steel cylinders) directly into milk of lime. Sometimes a solution of bleaching powder is treated with solutions of sodium, magnesium, or aluminium sulphates, when strong bleaching solutions of sodium hypochlorite, magnesium hypochlorite, or aluminium hypochlorite are obtained. These solutions bleach in alkaline solution somewhat more rapidly than bleaching powder (calcium hypochlorite) solution, but they cannot be obtained in the solid form (see, however, p. 47).

Use of Bleaching Powder as a Disinfectant.—A solution of bleaching powder is a very valuable disinfectant. One part of bleaching powder will, in three hours, sterilise 2,000 parts of ordinary sewage.

Electrolysed brine (see p. 54) has been used as a disinfecting fluid. It is claimed that it is cheaper (even if produced by the local authority) and more effective than most other materials.

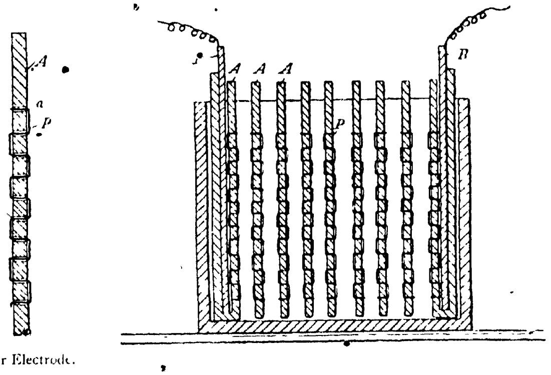
Electrolytic Bleaching.—When an electric current is passed through a solution of common salt without the intervention of a diaphragm, so that the liquids around the cathode and the anode are free to mix, we do not get chlorine gas evolved as such, but rather a solution of sodium hypochlorite is produced by the interaction of the nascent chlorine evolved at the anode and the caustic soda produced at the cathode, thus:—

$$2NaOH + 2Cl = NaCl + NaOCl + H_2O.$$

This solution may then be run off immediately and used for bleaching purposes.

Within the last twenty years this method has largely displaced the use of bleaching powder in certain works, and the process is said to be rapidly extending. The process was first brought to a commercially successful issue by Hermite and Kellner, and on the Continent the plants most in use are those of Schuckert, Kellner, and Ottel.

It is usual to electrolyse a 10 per cent. neutral salt solution, keeping the liquid cool by special arrangements. The best electrodes to use are platinum-iridium (since hypochlorites attack most other substances rapidly), and for success it is essential that the electric current "density" should be about 1,000-1,500 amperes per square métre electrode surface. At first a yield of hypochlorite of over 90 per cent. is obtainable by the electric current employed, but this soon sinks (on account of the reducing action of the evolved hydrogen at the cathode) until it becomes impossible, without the expenditure of very large amounts of electrical energy, to obtain solutions containing more than 3 per cent. of available chlorine. With low current densities much of the hypochlorite is reduced by the nascent hydrogen evolved at the cathode to chloride, $NaClO + 2H = NaCl + H_2O$, whilst at the anode the $NaClO$ tends to oxidise to $NaClO_3$ (see p. 36). Much better yields are obtained when some $CaCl_2$ is added to the solution, and when concentrated NaCl solutions are used. For example, a 20 per cent. NaCl solution can yield a liquid containing 3 per cent. available chlorine, with a yield of 50 per cent. of that theoretically obtainable from the current employed, whereas a 10 per cent. NaCl solution, with the same expenditure of current, will only give a liquid containing 2 per cent. available chlorine. However, the concentrated NaCl solutions use up more NaCl than the more dilute, and in practice it seems to be more economical to employ 10 per cent. solutions rather than more concentrated ones. Moreover, careful cooling of the liquid must be resorted to, otherwise a great loss of hypochlorite results owing to its conversion into chlorate (see p. 36).



Bipolar Electrode.

FIG. 26.—Kellner's Electrolytic Cell for Hypochlorites.

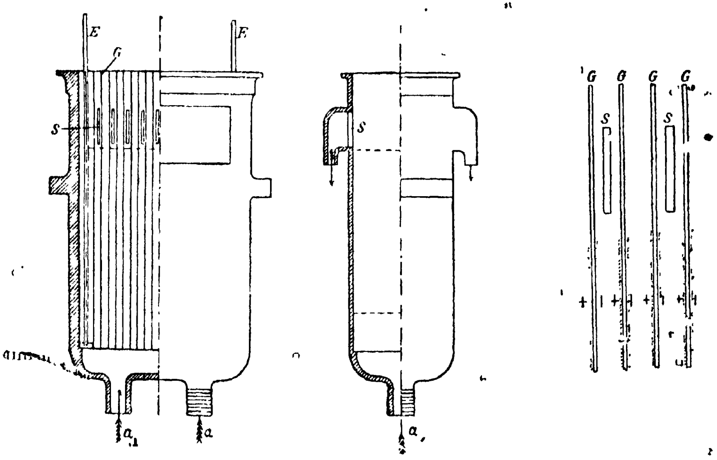
The subject of the formation and preservation of hypochlorites in solution was attacked by Muspratt and Smith in 1898 and 1899. By passing chlorine into the strongest possible solution of NaOH, they obtained needle-shaped crystals of the formula $NaClO.6H_2O$. They showed that in order to obtain a highly concentrated solution of hypochlorite the temperature must not exceed 27° C. and alkali must be always present in excess, and be so concentrated that any NaCl formed is precipitated (NaCl and KCl are very insoluble to concentrated NaOH or KOH solutions, see p. 24). They showed that solutions containing more than 35 g. available chlorine per 100 c.c. will not keep. The presence of iron salts causes the decomposition of concentrated hypochlorite solutions, attended by the evolution of oxygen and the formation of soluble sodium ferrate; in general, other salts did not cause this oxygen solution.

Other workers who have investigated the subject are Forster and Jorre, Lunge and Landolt (see *Journ. Pract. Chem.*, 2, **59**, 53; **63**, 141); and Sünder (*Bull. Soc. Ind.*, Mulhouse, **72**, 255), who claims that the decomposition of sodium hypochlorite solutions, which is occasionally met with when a solution of bleaching powder is decomposed with sodium carbonate, is due to the presenc of sodium bicarbonate as an impurity, 5 per cent. of bicarbonate sufficing to completely decompos a solution of NaOCl in the course of twenty-four hours in a manner not yet understood; in orde to obviate this decomposing action it is necessary that some free NaOH solution should be present.

We will now briefly describe some of the more successful apparatus in use fo producing electrolytic bleaching liquids.

Kellner's Process.—This is one of the oldest and most successful processes (see German Patents, 99,880, 1894, and 104,442, 1896). The electrodes consist of glass or non-conducting plates covered over with wire, bands or strips of platinum-iridium alloy. A non-conducting plate A (Fig. 26) of glass or similar material has its surface penetrated by numerous holes, *a,a,a,a*, through which fine platinum-iridium wire is drawn so that the surface of the plate looks as if it were covered with a wire network. The holes are then carefully cemented up with non-conducting material. In some forms of this apparatus the glass plates are simply wound round with platinum wire.

The plates so formed are placed vertically in a stoneware or glass trough, side by side, as shown in Fig. 26, only a narrow space being left between the successive plates. These plates slide into vertical grooves in the sides of the trough, so as to divide the cell into a number of compartments. The whole apparatus is filled with NaCl solution, and an electric current is led through the liquid by means of two conducting plates E,E, placed at the extreme ends of the apparatus. Fig. 27 shows a modern form of this electrolytic cell. The brine enters through two inlets *a,a* placed at the bottom of the vessel, and flows up between the wire-covered plates G,G,G, which form the electrodes, escaping through the slits S,S in the walls of the trough. E,E are the two terminal electrodic plates where the current enters and leaves the apparatus. The brine flowing up from the bottom of the cell from *a,a* between the wire-covered plates G,G,G,G is subjected to the action of an electric current flowing between each pair of plates, and thus a considerable amount of hypochlorite is produced. The brine used is usually 10 per cent. NaCl solution, and the drop in the voltage between each two successive plates of the apparatus is usually some 5-6 volts; in the apparatus just illustrated (in which there are twenty cells) the potential difference between the end electrodes E,E is usually about 110 volts, with a current of 120 amperes. One of the intermediate wire-covered plates of the apparatus requires some 150 m. of platinum-iridium wire of 0.1 mm. diameter, or 75 m. on each side of the plate.



Longitudinal Section Side View Bipolar Electrodes

FIG. 27 Modern Form of Kellner's Electrolytic Cell.

It can be shown that this use of thin wire gives an extraordinary high current density. *E.g.*, if we assume that only half the surface of the wire is effective (viz., that facing the opposite electrode of a cell), and neglecting the parts of wire in the grooves and other non-effective parts of the plates, we will see that the effective surface carrying the current of 120 amperes is only 0.1177 sq. m., giving a density of 10,200 amperes per square metre. This high current density is an essential condition for success in producing hypochlorites.

The method of using this electrolytic cell, *e.g.*, for bleaching purposes in the textile industry, is indicated in Figs. 28 and 29, which gives the plant of *Siemens and Halske*. S is a chamber filled with salt through which a stream of water trickles. The brine solution thus obtained flows out at the bottom of the salt holder, through a filter cloth, and then through a leaden pipe *a*, into a tank M, where it is mixed with water in any required volume in order to bring the brine solution up to its correct strength for use. From M mixed brine is let down into the storage reservoir N. By means of a tap K it is from time to time allowed to fill a tank P, which contains a cooling worm of hard lead (so that the brine in P can be kept at as low a temperature as is convenient). Just above P is fixed the electrolytic cell E, which we have just described. Through the electrolytic cell E the centrifugal pump (Fig. 29) sucks the brine along the pipe *b* and then forces it through the pipe *i* (the tap C being turned so as to shut off the pipe D

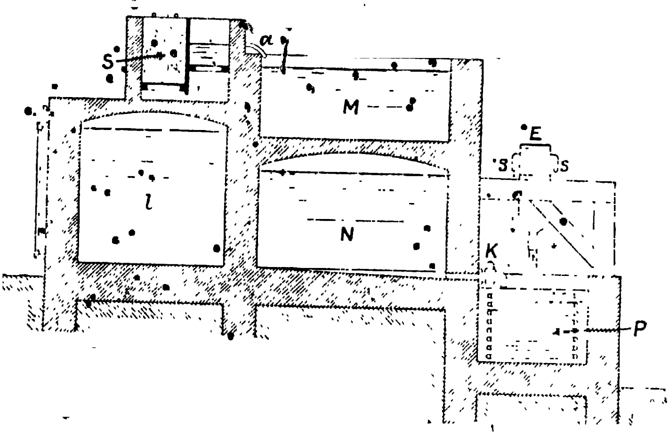


Fig. 28.—Siemen's and Halske's Apparatus for Electrolytic Bleaching.

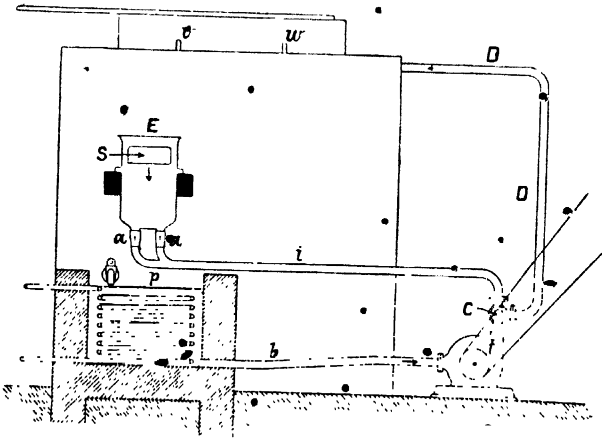
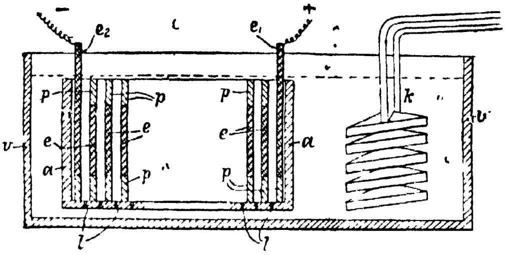


Fig. 29.—Siemen's and Halske's Apparatus for Electrolytic Bleaching.

into the bottom of the electrolyser E, where it rises up between the wire-covered plates; and, after being subjected to the action of the electric current, flows out of the apparatus through the slits s in the sides, the liquid falling back again into the tank P. The circulation of brine through the electrolyser E is maintained until the proper percentage of active chlorine is attained, when the tap C is turned so as to cut off *i* and the electrolyser E, at the same time opening communication between the pipes D,D and *b*. The pump then forces the active



Longitudinal Section.

FIG. 30.—Haas and Ottel's Cell for Electrolytic Bleaching.

brine out of the tank P, up through D into the storage tank *l*, where it is run off, as required, for bleaching purposes.

A considerable number of firms in the paper trade and textile industry use this plant, especially in Germany.

Haas and Öttel's apparatus (see the German Patents, 101,296, of 17th May 1896, and 114,739, of 3rd February 1900) consists of two earthenware vessels, one a large one *v,v* and the other a smaller one *a,a*, placed within the large vessel just below the level of the brine which fills the large vessel. The smaller interior vessel *a,a* has a number of wire electrodes, as in the previous system, stretched over a number of vertical plates. *e,e,e* show these electrodes, which are separated from the base of the vessel and the top by non-conducting supports, *p,p*. e_1e_2 are

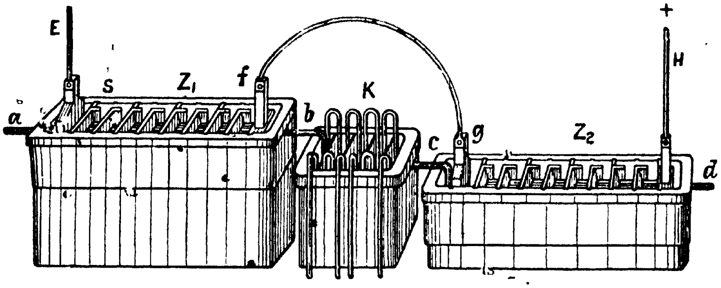
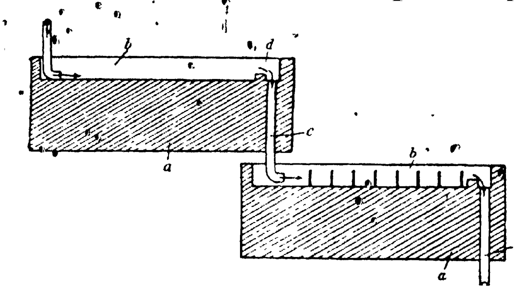


FIG. 31.—Schuckert's Cell for Electrolytic Bleaching.

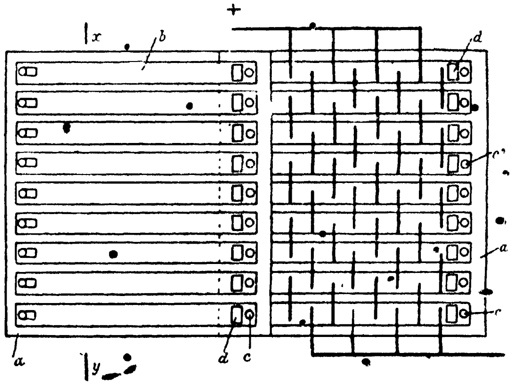
the two terminal electrodes through which the current flows. Between each compartment of the interior vessel *a,a* is a small hole *l*, which maintains communication between the brine in the outer vessel *v,v* and that in the interior vessel. The action is as follows:—The current, entering at e_1 and emerging at e_2, flows through the successive electrolytic compartments of the interior vessel, and the brine is electrolysed. Partly owing to the rise of temperature produced by the passage of the electric current through the liquid, and partly owing to the rise of hydrogen bubbles, the brine inside the successive compartments of the interior vessel becomes specifically lighter than the brine in the exterior vessel, and rises up to the surface between the walls of the compartments of the interior vessel. Thus a current is produced, cold brine from outside entering the holes *l*,*l* at the bottom of the interior vessel, rising up between the electrolytic plates of the interior vessel, and escaping at the surface; thus all the brine in the exterior vessel in time streams through the interior vessel and is electrolysed. The cooling coil *k* keeps the brine in the exterior vessel as cool as possible.



Longitudinal Section

FIG. 32.—Schoop's Electrolyser.

Fig. 31 shows **Schuckert's** apparatus, as used by the Siemens-Schuckert Werke. This is also stated to be very successful in practice. The two stoneware troughs z_1 and z_2 each contain nine cells, each with an electrode of platinum wire (+ pole) and a graphite (−) electrode. The current passes in at H and comes out at the terminal E, the tension between H and E being about 110 volts, which, distributed over the eighteen cells, gives a voltage through each cell of 6 volts. A 10 per cent. NaCl solution flows in at *a*, and passes in a continual stream right through the cell, emerging again at *d*, where it passes away. It is found advisable to add a little $CaCl_2$ solution and some sodium rosinate to the liquid. After passing out from z_1 the liquid, before entering the second trough z_2, flows through an intermediate trough K, where it is thoroughly cooled by the cooling coils represented



Ground Plan.

FIG. 33.—Schoop's Electrolyser.

as dipping into the various compartments of K. The liquid emerging at *d* finally contains some 2 per cent. of active chlorine, and for use the liquid is diluted with water until it contains some 0.2-0.5 per cent active chlorine. The apparatus is described in the German Patent, 141,724 (1902).

Schoop's Apparatus, as described in the German Patents, 118,450, of 1899, and 121,525, of 1900, electrolyses a stream of brine gradually flowing down a number of narrow channels, the walls of which contain the electrodes, formed of fine foil projecting into each chamber (see Figs. 32, 33). The process is successfully worked in several works in Germany.

Other processes, all of which have been practically worked with more or less success, are described in the German Patents:—

K. Kellner, D.R.P., 165,486, of 6th November 1902; W. Kother, D.R.P., 180,562, of 15th August 1905; A. Vogelsang, D.R.P., 205,110, of 9th March 1906; G. Thiele, D.R.P., 205,087, of 11th July 1906 (who adds to the NaCl solution some $CaCl_2$ and an organic sulphur compound (not aromatic) of high molecular weight, thereby obtaining a liquid with over 5 per cent. active chlorine in it).

Solid Sodium Hypochlorite, containing 60 per cent. available Cl, and melting at 43° C., has been prepared (see Muspratt, *Journ. Soc. Chem. Ind.*, 1903, p. 592. See also p. 49).

Hypochlorites as Disinfectants.—Like bleaching powder (p. 48) hypochlorites can be used for disinfecting purposes, a solution containing 10 per cent. of available chlorine being twenty-five times as effective as phenol.

Recently Dr Dakin and Dr Carrel have used hypochlorites with success in treating wounds. A solution of sodium hypochlorite, carefully neutralised with boric acid to remove alkalinity, and to reduce the irritant action of the original solution, very rapidly dissolves away necrotic tissues and sterilises even very badly infected wounds. This cheap and powerful disinfectant is very easily prepared.

CHAPTER VI

The Manufacture of Hydrochloric Acid

CHAPTER VI

THE MANUFACTURE OF HYDROCHLORIC ACID

LITERATURE

LUNGE.—"Sulphuric Acid and Alkali." 1915.
T. MEYER.—"Sulfat und Salzsaure." 1907.
F. HURTER.—*J. Soc. Chem. Ind.*, 1885, 639; 1887, 707; 1893, 226
LASCHE.—*Z. angew. Chem.*, 1894, **6**, 610, *cf.* p. 614.
GEOFFREY MARTIN.—"Industrial Chemistry," Vol II. 1915

Manufacture of Hydrochloric Acid.—Hydrochloric acid is usually manufactured by heating two molecular proportions of salt with one molecular proportion of concentrated sulphuric acid. Usually about half a ton of salt is placed in a large semispherical pan set in brickwork and heated by direct firing. An equal weight of concentrated sulphuric acid (1.7 sp. gr.) is added from a leaden cistern, when the following action takes place:—

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

About 70 per cent. of the hydrochloric acid escapes through a flue in the dome of brickwork which covers the pan, and is condensed by water as is described below. The fused mass is finally raked into another part of the furnace, and is there heated to redness, when the action is carried to completeness, thus:—

$$NaHSO_4 + NaCl = Na_2SO_4 + HCl$$

The hydrochloric acid escapes through a separate flue. This is known as the **Salt Cake Process**, and details of the furnaces, etc., are given fully in Martin's "Industrial Chemistry," Vol. II.

The main product is sodium sulphate, the hydrochloric acid being more or less a by-product.

The second process of manufacturing hydrochloric acid is known as **Hargreave's Process**, and consists in passing a mixture of sulphur dioxide, air, and steam over salt heated to dull redness, when the following action takes place:—

$$2NaCl + SO_2 + O + H_2O = Na_2SO_4 + HCl.$$

The process is fully described under "Sodium Sulphate" in "Industrial Chemistry," Vol. II.

The hydrochloric acid gas evolved in the manufacture of sodium sulphate, either by the salt cake process or the Hargreave's process, is always absorbed by being led into water.

At one time the acid fumes from the salt cake furnaces were allowed to escape into the air. In spite of enormous chimneys reaching to the height of 450 ft. and more, the neighbourhood of the salt cake factories was surrounded by dense clouds of smoke. The acid vapours in the air killed the vegetation for miles around the factories, and brought great distress to farmers. Consequently, in 1863 the Alkali Act was passed which makes it compulsory for 95 per cent. of the escaping acid gases to be condensed. The exit gases should not contain more than 0.2 grain HCl per cubic foot, and the total amount of acid gases escaping must be less than is equivalent to 4 grains of SO_3 per cubic foot.

This at first caused great expense to the factories, as at that time HCl was an almost worthless by-product; but soon the rise in value of HCl for the manufacture of chlorine and bleaching powder made the forcible condensation process an actual source of gain, and at the present time it is common for 99.27 per cent. of the HCl to be condensed.

Fig. 34 shows a typical plant attached to salt cake furnaces, giving 4,800 kg. of sodium sulphate per twenty-four hours. The HCl gas escapes from the salt cake furnaces A, A_1 by means of two separate pipes. One pipe B, made out of acid-proof earthenware, leads the concentrated and fairly cool HCl gas out of the "pan" in A; while the other pipe B_1 leads the hot dilute HCl gas out of the muffle or roasting part of the furnace. This HCl gas is dilute and very hot, and so the first part of the pipe B_1 is made of tarred sandstone. The gases pass into two sandstone towers C, C_1 where they receive a preliminary cooling, and are to a great extent freed from dust and sulphuric acid. They then pass through a series of some 50 to 60 acid "receivers." These are simply large "Woulff's bottles," made of acid-proof stoneware, about 32-37½ in. high, connected together by wide ∩-shaped pipes, and arranged as shown in two parallel rows. They are laid down so that a gentle inclination on slope towards the furnaces exists, so that a stream of water can flow through the series in a direction opposite to that of the gases coming from the furnace. The holes for the water are well seen in Fig. 35. This water absorbs most of the HCl, and is run off into the side receivers G_1, G.

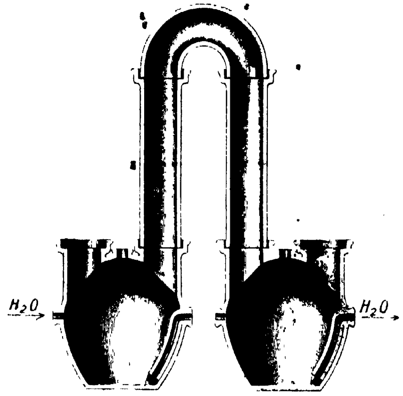


FIG. 35.—Hydrochloric Acid Receivers.

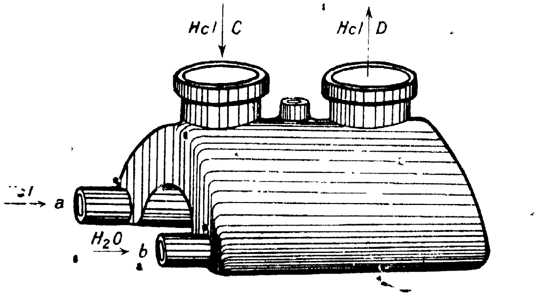


FIG. 36.—Cellarius Receivers.

In Germany the more efficient Cellarius receivers have come into use of late years.

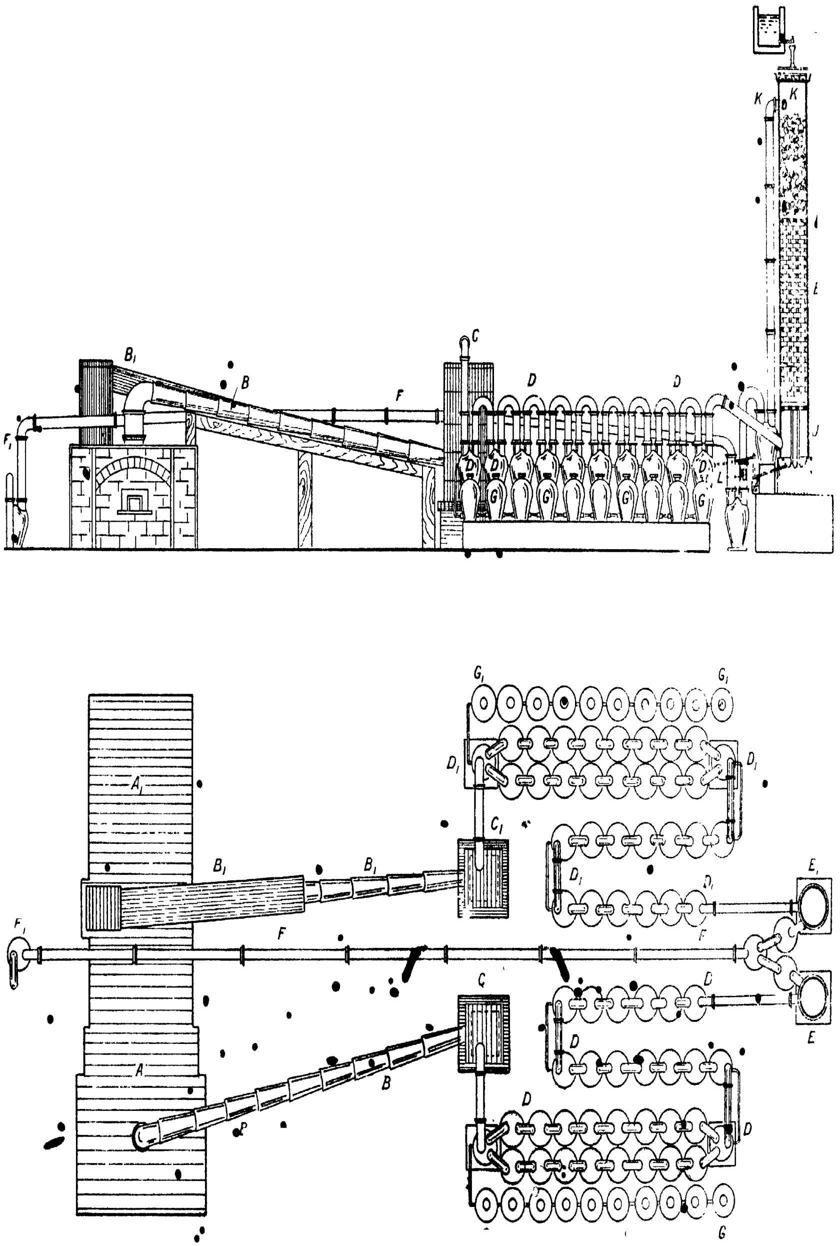

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FIG. 7.—Plant for Manufacture of Hydrochloric Acid.

[To face page 58.

Fig. 36 shows a typical Cellarius receiver. The gas enters at C and escapes at D, while the absorbing water enters by the pipe *g*, flows over the "saddle" and escapes by the pipe *b*. Thus a much larger absorption surface is presented to the entering gas, and the latter is more thoroughly mixed with the water and cooled. The whole vessel is immersed in tanks filled with cold water which thus greatly increases the efficiency of the absorption and the strength of acid produced.

The gases finally escaping from the terminal receivers now pass into absorption towers E, E$_1$, where they meet a stream of descending water which removes the last traces of acid from the gas.

An absorption tower of improved construction is shown in Fig. 34. It consists of a series of rings of hard earthenware, about 1 m. in diameter, set one on the other so as to form a tower some 15-30 m. high. The upper part of the tower is filled with coke, and the lower part with stoneware plates or bricks. From the water tank H a stream of water is sprinkled by means of a rotating "sparger" over the coke and flows in a steady stream down the tower, escaping at the bottom into the stoneware receivers described above.

The gas from the receivers enters at J (Fig. 34) at the bottom of the tower, and escapes at K into a long earthenware tube F F$_1$, which leads the now acid free gas away to the chimney. At L samples of the acid can be withdrawn and tested.

In England in many works it is the custom to pass the gases evolved from the salt cake furnaces directly into the absorption towers, without the introduction of the elaborate system of cooling and absorption vessels described above. These condensing towers are some 20-30 m. high, and are filled with coke or bricks down which a stream of water trickles as previously described. They are usually built of sandstone plates previously boiled in tar or asphalt, made air and water tight with a lute made of tar and clay, and securely bolted together by means of iron clamps and bars. The aqueous acid thus obtained is not quite so strong as that obtained with the more elaborate condensing system, because the gases enter the tower while still hot. The acid, too, is more impure, being contaminated with organic matter, sulphur dioxide, sulphuric acid, chlorine, chlorides of iron and arsenic, the latter substances sometimes being present in considerable quantities, being derived from the pyrites used in making the sulphuric acid used. Within recent years, acid-resisting materials such as silicon iron alloys (tantiron, ironac, duriron, etc.), fused silica, acid-proof earthenware, etc., have been widely introduced in constructional details of acid plant.

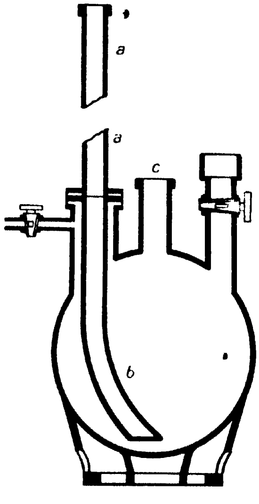

FIG. 37. Acid "Egg."

The main problem now before hydrochloric acid factories is not so much the condensation of all the HCl fumes, but how to condense them in such a manner as to yield **only strong acid** (the only sort saleable), and by the method first described the condensation is now so perfect that it is possible to recover some 99.27 per cent. of the evolved HCl, mostly in the form of strong acid of 21° Bé. The strength of the produced aqueous acid depends upon the concentration of the gas and the temperature at which it enters the absorbing water.

For example, a 100 per cent. by volume HCl gas at 0° C. gives an aqueous acid containing 45.2 per cent. by weight HCl; while a 5 per cent. HCl gas under the same conditions will only yield an aqueous acid containing 36 per cent. by weight HCl (22° Bé.), and a 10 per cent. HCl gas (by volume) will only yield a 39 per cent. by weight HCl solution (24° Bé.).

As the temperature of the entering gases increases, so also the strength of the obtainable acid decreases. *E.g.*, a 5 per cent. by volume HCl gas at 20° C. will only yield an aqueous acid containing 33 per cent. HCl by weight (20° Bé.).

The conditions affecting the condensation of HCl have been described at length by F. Hurter (*J. Soc. Chem. Ind.*, **1885**, 639; **1887**, 707; **1893**, 226) and the reader should consult these papers for further information (see also Lasche, *Z. angew. Chem.* (1894), **6**, 610; Lunge, same journal, p. 615).

The problem of the complete condensation of the HCl gases evolved in the manufacture of salt cake is first of all complicated by the fact that these gases contain very variable amounts of HCl. *E.g.*, the HCl gases from Hargreave's and the "open coaster" furnaces may contain much less than 10 per cent. by volume of HCl. Secondly, the cooling down of the gases during the condensing process is rendered difficult by the fact that when the gas dissolves in water it evolves much heat, so that as the cold absorption water is forced against the current of hot gases it rapidly becomes heated, and so does not dissolve the maximum amount possible of HCl. However, the introduction of modern pumps made of stoneware, ebonite, or acid-resisting iron now enables the manufacturers to pump the liquid in a continual stream through the condensing system, and so they can ultimately obtain an acid of 20° Bé. even out of weak HCl gases, such as are evolved from Hargreave's process. The introduction of these acid pumps betokens a great advance on the old system of manufacture.

The acid is best elevated by acid pumps or elevators as described in Martin's "Industrial Chemistry," Vol. II., under **Sulphuric Acid.**

The acid is also elevated sometimes in "emulsators," where it is blown mixed with compressed air in the form of a froth from one vessel to another. The old acid "egg" (Fig. 37) still maintains its position as a simple acid elevator but is very wasteful compared with "elevators" and acid pumps. Compressed air forced in at *c* forces the acid contained in the vessel up the tube *ab*.

These "eggs" are sometimes made of strong thick-walled stoneware, which, however, is liable to fracture under a sudden accidental blow.

Casing iron with ebonite is efficient but very costly. Lately there have been placed on the market non-corroding iron alloys such as "tantiron," "ironac," etc., often made of iron mixed with silicon and other components—which are stated to be extremely efficient, as regards their non-corrodibility and their strength. For HCl.aq., however, it is always best to use proper acid pumps for elevating.

Transport and Storage.—The acid is usually transported in large glass "carboys" or in stoneware vessels some 1-1½ m. high. Occasionally ebonite-lined iron vessels or vessels made of guttapercha have been used. HCl is now being transported in railway tank waggons lined with specially prepared waxed wood.

One of the great difficulties of the industry has been the expense of the vessels necessary for storing large quantities of HCl for any length of time, all the more so as more hydrochloric acid is made than is required in industry and so the price is low. The cause of this is the fact that there is a great demand for sodium sulphate, and the accompanying HCl simultaneously produced more than suffices for the demand for the acid.

Where hydrochloric acid is required in places remote from alkali works, it is usually manufactured by the action of sulphuric acid upon salt in special cast-iron cylinders fitted with sandstone doors. This acid is condensed as already described. It is usually much purer than the acid from alkali works and is known in the trade as cylinder acid in contradistinction to "tower" acid which contains more sulphuric acid.

Good commercial cylinder acid should not contain more than 0.5 per cent. of H_2SO_4.

Purification of the Acid.—The purification of the acid from the various impurities which it contains (*e.g.*, arsenic, sulphuric acid, SO_2, iron chloride, etc.) is usually carried out in special factories.

Arsenic is detected by means of Marsh's test or by adding stannous chloride, which produces a dark precipitate of arsenic. Arsenic may be removed by adding stannous chloride, settling the precipitate, and redistilling the liquid. Arsenic-free HCl is best obtained by employing arsenic-free materials to start with, but it is often removed technically in great parts by washing the acid with tar oils. **Sulphuric acid** is detected by adding $BaCl_2$ solution to the dilute acid, when a white precipitate of $BaSO_4$ is produced if it is present. Sulphuric acid is largely eliminated during the process of condensation, but may be completely removed by adding the proper amount of $BaCl_2$ and distilling.

Sulphur dioxide, SO_2, is detected by adding zinc to the diluted acid, when sulphuretted hydrogen, H_2S, is given off and is detected by its blackening effect on lead acetate paper. **Free iodine** is found by adding KI and starch solution to the diluted acid, when a blue colour is produced.

The complete purification of the acid from these impurities is a matter of great difficulty, and where pure acid is essential it is easiest to start with pure sulphuric acid and pure salt and thus exclude the foreign impurities. When chemically pure HCl is required it is usually distilled in platinum stills.

Technical Uses of Hydrochloric Acid.—In England the main use of concentrated hydrochloric acid is for making chlorine for the manufacture of bleaching powder, chlorates, etc. The acid sold is usually 20°-22° Bé., acids weaker than this scarcely getting a market. In Germany and also in Great Britain large quantities of concentrated hydrochloric acid are absorbed in the colour industry, metallurgical industries, and for very many minor industrial purposes. For example, dilute HCl is largely used for purifying coke, iron ores, clay, for regenerating exhausted animal charcoal, for preparing CO_2 in the aerated water industry, for "pickling" sheet iron in the galvanising industry, so as to remove rust and leave a clean surface for the zinc to adhere to. Also for the manufacture of certain chlorides, in making pottery, and in numerous other things as well. One curious application may be mentioned, viz.: the making of freezing mixtures of concentrated HCl and snow, or sodium sulphate.

The acid is also used in analytical chemistry as a solvent, and for titrating purposes. "Aqua regia"—a mixture of HCl and HNO_3—is also made for dissolving gold and making gold chloride, which finds considerable use in photography.

Properties of Aqueous HCl.—The pure concentrated aqueous acid is a colourless liquid fuming strongly in air. One volume of water at 0° absorbs 503 volumes of HCl gas. The following table due to Roscoe and Dittmar (*Journ. Chem. Soc.*, 1860, 128) gives the weight of gas absorbed by 1 g. of water at different temperatures:—

Temperature.	Grams HCl Absorbed by 1 g. H_2O	Temperature.	Grams HCl Absorbed by 1 g. H_2O.	Temperature.	Grams HCl Absorbed by 1 g. H_2O.
0°	0.825	24°	0.700	44°	0.618
4°	0.804	28°	0.682	48°	0.603
8°	0.783	32°	0.665	52°	0.589
12°	0.762	36°	0.649	56°	0.575
16°	0.742	40°	0.633	60°	0.561
20°	0.721				

When HCl dissolves in water, 17,314 calories are evolved per gram-molecule of HCl dissolved. The composition of the aqueous acid changes when boiled, according to the temperature and pressure employed; but corresponding to a definite pressure a constant boiling mixture of HCl and water is obtained. The aqueous acid which boils unchanged at 110° C. at 760 mm. contains 20.24 per cent. HCl (Roscoe and Dittmar, *loc. cit.*). A weaker solution when evaporated at ordinary pressures concentrates to this strength. A stronger acid loses HCl and also attains this strength when evaporated.

The following table gives the specific gravity of solutions of aqueous hydrochloric acids of given strengths, as given by Lunge and Marchlewski (*Zeit. angew. Chem.*, 1891, 133).

SPECIFIC GRAVITY OF PURE HYDROCHLORIC ACID SOLUTIONS AT 15° C. (REDUCED IN VACUO), AFTER LUNGE AND MARCHLEWSKI.

Sp. Gr. at 15/4° C.	Degrees Baumé.	Degrees Twaddle.	100 Parts by Weight Correspond to the Following Amount of Pure Acid per Cent.						1 Litre Contains in Kilogrammes.					
			Pure HCl.	18° Bé. Acid.	19° Bé. Acid.	20° Bé. Acid.	21° Bé. Acid.	22° Bé. Acid.	Pure HCl.	Acid of 18° Bé	Acid of 19° Bé.	Acid of 20° Bé.	Acid of 21° Bé.	Acid o 22° Bé
1.000	0.0	0.0	0.16	0.57	0.53	0.49	0.47	0.45	0.0016	0.0057	0.0053	0.0049	0.0047	0.004
1.005	0.7	1	1.15	4.08	3.84	3.58	3.42	3.25	0.012	0.041	0.039	0.036	0.034	0.033
1.010	1.4	2	2.14	7.60	7.14	6.66	6.36	6.04	0.022	0.077	0.072	0.067	0.064	0.061
1.015	2.1	3	3.12	11.08	10.41	9.71	9.27	8.81	0.032	0.113	0.106	0.099	0.094	0.089
1.020	2.7	4	4.13	14.67	13.79	12.86	12.27	11.67	0.042	0.150	0.141	0.131	0.125	0.119
1.025	3.4	5	5.15	18.30	17.19	16.04	15.30	14.55	0.053	0.188	0.176	0.164	0.157	0.149
1.030	4.1	6	6.15	21.85	20.53	19.16	18.27	17.38	0.064	0.225	0.212	0.197	0.188	0.179
1.035	4.7	7	7.15	25.40	23.87	22.27	21.25	20.20	0.074	0.263	0.247	0.231	0.220	0.209
1.040	5.4	8	8.16	28.99	27.24	25.42	24.25	23.06	0.085	0.302	0.283	0.264	0.252	0.240
1.045	6.0	9	9.16	32.55	30.58	28.53	27.22	25.88	0.096	0.340	0.320	0.298	0.284	0.270
1.050	6.7	10	10.17	36.14	33.95	31.68	30.22	28.74	0.107	0.380	0.357	0.333	0.317	0.302
1.055	7.4	11	11.18	39.73	37.33	34.82	33.22	31.59	0.118	0.419	0.394	0.367	0.351	0.333
1.060	8.0	12	12.19	43.32	40.70	37.97	36.23	34.44	0.129	0.459	0.431	0.403	0.384	0.365
1.065	8.7	13	13.19	46.87	44.04	41.09	39.20	37.27	0.141	0.499	0.469	0.438	0.418	0.397
1.070	9.4	14	14.17	50.35	47.31	44.14	42.11	40.04	0.152	0.539	0.506	0.472	0.451	0.428
1.075	10.0	15	15.16	53.87	50.62	47.22	45.05	42.84	0.163	0.579	0.544	0.508	0.484	0.460
1.080	10.6	16	16.15	57.39	53.92	50.31	47.99	45.63	0.174	0.620	0.582	0.543	0.518	0.493
1.085	11.2	17	17.13	60.87	57.19	53.36	50.90	48.40	0.186	0.660	0.621	[illegible]	0.552	0.523
1.090	11.9	18	18.11	64.35	60.47	56.41	53.82	51.17	0.197	0.701	0.659	0.615	0.587	0.558
1.095	12.4	19	19.06	67.73	63.64	59.37	56.64	53.86	0.209	0.742	0.697	0.650	0.620	0.590
1.100	13.0	20	20.01	71.11	66.81	62.33	59.46	56.54	0.220	0.782	0.735	0.686	0.654	0.622
1.105	13.6	21	20.97	74.52	70.01	65.32	62.32	59.26	0.232	0.823	0.774	0.722	0.689	0.655
1.110	14.2	22	21.92	77.89	73.19	68.28	65.14	61.94	0.243	0.865	0.812	0.758	0.723	0.687
1.115	14.9	23	22.86	81.23	76.32	71.21	68.93	64.60	0.255	0.906	0.851	0.794	0.757	0.719
1.120	15.4	24	23.82	84.62	79.53	74.20	70.79	67.31	0.267	0.948	0.891	0.831	0.793	0.754
1.125	16.0	25	24.78	88.06	82.74	77.19	73.64	70.02	0.278	0.991	0.931	0.868	0.828	0.788
1.130	16.5	26	25.75	91.50	85.97	80.21	76.52	72.76	0.291	1.034	0.972	0.906	0.865	0.822
1.135	17.1	27	26.70	94.88	89.15	83.18	79.34	75.45	0.303	1.077	1.011	0.944	0.901	0.856
1.140	17.7	28	27.66	98.29	92.35	86.17	82.20	78.16	0.315	1.121	1.053	0.982	0.937	0.891
1.1425	18.0	..	28.14	100.00	93.95	87.66	83.62	79.51	0.322	1.143	1.073	1.002	0.955	0.908
1.145	18.3	29	28.61	101.67	95.52	89.13	85.02	80.84	0.328	1.164	1.094	1.021	0.973	0.926
1.150	18.8	30	29.57	105.08	98.72	92.11	87.87	83.55	0.340	1.208	1.135	1.059	1.011	0.961
1.152	19.0	.	29.95	106.43	100.00	93.30	89.01	84.63	0.345	1.226	1.152	1.075	1.025	0.975
1.155	19.3	31	30.55	108.58	102.00	95.17	90.79	86.32	0.353	1.254	1.178	1.099	1.049	0.997
1.160	19.8	32	31.52	112.01	105.24	98.19	93.67	89.07	0.366	1.299	1.221	1.139	1.087	1.033
1.163	20.0		32.10	114.07	107.14	100.00	95.39	90.70	0.373	1.326	1.246	1.163	1.109	1.054
1.165	20.3	33	32.49	115.46	108.48	101.21	96.55	91.81	0.379	1.345	1.264	1.179	1.125	1.070
1.170	20.9	34	33.46	118.91	111.71	104.24	99.43	94.55	0.392	1.391	1.307	1.220	1.163	1.106
1.171	21.0		33.65	119.58	112.35	104.82	100.00	95.09	0.394	1.400	1.316	1.227	1.171	1.113
1.175	21.4	35	34.42	122.32	114.92	107.22	102.28	97.26	0.404	1.437	1.350	1.260	1.202	1.143
1.180	22.0	36	35.39	125.76	118.16	110.24	105.17	100.00	0.418	1.484	1.394	1.301	1.241	1.180
1.185	22.5	37	36.31	129.03	121.23	113.11	107.90	102.60	0.430	1.529	1.437	1.340	1.279	1.216
1.190	23.0	38	37.23	132.30	124.30	115.98	110.63	105.20	0.443	1.574	1.479	1.380	1.317	1.252
1.195	23.5	39	38.16	135.61	127.41	118.87	113.40	107.83	0.456	1.621	1.523	1.421	1.355	1.289
1.200	24.0	40	39.11	138.98	130.58	121.84	116.22	110.51	0.469	1.667	1.567	1.462	1.395	1.326

CHAPTER VII

The Bromine Industry

CHAPTER VII

THE BROMINE INDUSTRY

LITERATURE

GEOFFREY MARTIN and ERNEST DANCASTER. "The Halogens." Vol. VIII of "Modern Inorganic Chemistry." Edited by Newton Friend. 1915.

SMALL quantities of bromine occur in many silver ores, but much greater quantities occur associated with potassium, magnesium, calcium, sodium, etc., in various mineral waters, springs, and in sea water. The waters of the Atlantic Ocean contain 0.007 per cent. Br, while in the Dead Sea 0.42 g. Br per litre is present. However, the largest sources (and practically the only technical sources) are the saline deposits of Stassfurt, which contain about 1 per cent. of magnesium bromide, and the [redacted]ings in Ohio, which contain from 3.4-3.9 per cent. of magnesium bromide.

Manufacture.—The bulk of the bromine placed on the market is made at Stassfurt from the mother liquor remaining after the separation of the potassium salts contained in the salt deposits (see Martin's "Industrial Chemistry," Vol. II.). The residual mother liquor contains about 0.25 per cent. of bromine in the form of magnesium bromide, $MgBr_2$, from which the bromine is liberated by treating with chlorine:—

$$MgBr_2 + Cl_2 = MgCl_2 + Br_2$$

The apparatus now employed at the Leopoldshall Chemical Works (German Patent, 19,780, of 188[illegible]) is shown in Fig. 38 The bromide-rich mother liquors pour through the pipe *a* (which has a water seal at *m*), through a sandstone drum *b* over a perforated plate *e*, whereby it is uniformly distributed over the whole area of a tower A filled with glass or earthenware balls, which expose a large surface area to the percolating liquids.

A stream of chlorine gas, issuing from the still D (in modern works the still is replaced by a cylinder of liquid chlorine, which affords better control of the Cl), pours through the chamber B up the tube *d* (which is sufficiently wide to allow of the simultaneous passage of the chlorine gas to the tower A, and the waste liquors from A to the chamber B) into A, where it meets with the descending stream of bromide-rich liquors. Bromine vapour is set free, which, ascending, escapes by the tube O through the condenser E, and collects as a liquor in the bottles F, the last traces of bromine and chlorine being removed by the vessel G, which contains iron filings kept moist by a stream of water.

In order to free the waste liquor flowing away from A completely from all traces of bromine and fluorine, it is allowed to flow into the chamber B. In order to escape from B the liquor must flow over sandstone shelves in the direction of the arrows, and while so doing is subjected to a current of high-pressure steam blown into the apparatus through the pipe C. The chlorine and bromine are completely driven out of the liquid, escaping with the excess of steam up the pipe *d* into the tower A. The chlorine and bromine free liquid flows away by the pipe *i*.

An improvement on this apparatus has been patented by Wünsche and Sauerbrey (German Patent, 158,715), the apparatus consisting of cast-iron elements, of hexagonal section, lined with stoneware plates and provided with several thousands of specially designed contact bodies resting on gratings, the apparatus being so arranged that a perfect counter-current is attained. This apparatus requires 0.6 kg. of Cl for every 1 kg. of Br made. Only 3-5 kg. of Br in the form of iron bromide are necessary for removing the Cl from 100 kg. of the crude Br produced.

Kubierschky (German Patent, 194,567) has designed a very efficient plant of a somewhat different type (see Fig. 39). This consists of a tower lined with stoneware and divided into several superimposed compartments, which are provided with perforated plates. The divisions between the compartments are water sealed, so that liquids can pass, but not gas. The mother liquor, which has been previously heated, enters the tower at the top at A, and, in its descent, is met by the chlorine,

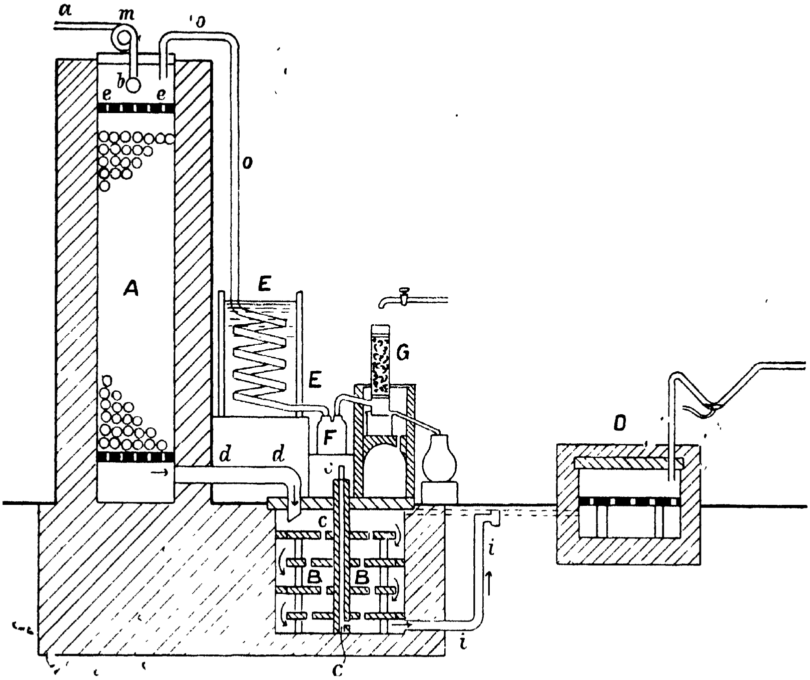

FIG. 38.—Bromine Plant of the Leopold Chemical Works.

which is introduced into the lower end C and passes upwards through the tubes, which are so arranged that the gas enters each compartment at the upper end, then descends, together with the hot mother liquor, and enters the vapour pipe leading into the next higher compartment, and so forth. Steam is introduced into the lower compartment, and follows the same course as the chlorine. By this arrangement undercurrents, which are certain to be formed when a direct upward current is used, are avoided. The bromine leaves the tower at B, and is condensed in an earthenware coil. It is then purified in the refining tower, in which it flows downwards into a vessel containing boiling bromine. Most of the chlorine is driven off through the [illegible], and the purified bromine is syphoned off.

In some American works the mother liquors, after the extraction of sodium chloride, are concentrated and distilled with sulphuric acid and potassium chlorate in stoneware retorts. The liberated bromine is condensed in lead condensers and purified by redistillation.

Manufacture by Electrolytic Process.—In this process mother liquors are electrolysed in open vessels, using carbon electrodes. The magnesium bromide $MgBr_2$, is decomposed by the electric current before the magnesium chloride. The bromine is thus separated.

Processes have been devised by Dow, Pemsel, Hopfner, Wünsche, Nahnsen, Kossuth, and others. Most employ diaphragms to effect the separation, with the exception of Kossuth. The liberated bromine remains dissolved in the liquid, and must be separated by distillation and purified.

Purification.—The crude bromine thus obtained is always purified by redistillation, small quantities of chlorine present being removed by the addition of ferrous bromine or calcium bromide, when the chlorine displaces the bromine from combination, setting the latter free.

Sometimes the liquid is purified without chemicals by fractional distillation (see German Patents, 174,848 and 205,448), the more volatile portions (1-4 per cent. of distillate) which contain any Cl or chlorine bromide being collected separately. If anhydrous Br is needed it is distilled over concentrated H_2SO_4. If I is present this is removed by treating with a Ca salt, Ca_2I_2 being precipitated.

In the preparation excess of chlorine should be avoided, otherwise much chlorine bromide is formed.

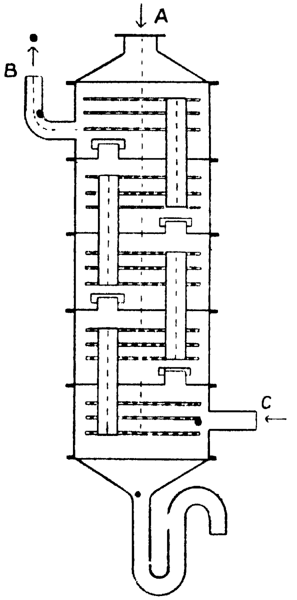

FIG. 39.—Kubierschky's Plant for Bromine Manufacture.

Properties of Bromine.—A heavy, mobile, dark red liquid of sp. gr. 3·1883 at 0° C. It freezes to a brown crystalline mass at −7° C. Boils at 59° C. The liquid has a disagreeable smell, attacking the eyes and the mucous membrane of throat and nose. It is poisonous, producing painful sores on the skin, which are difficult to heal.

100 g. of water dissolve 4.3 g. Br at 0° C., and 3.2 g. at 20° C., but it is much more soluble in organic liquids such as ether, carbon disulphide, chloroform, acetic acid, etc. It resembles chlorine in properties, but is not so energetic, and is displaced from its compounds by chlorine.

Uses.—Bromine is used fairly largely in the colour industry and other branches of synthetical organic chemistry, also in metallurgy, photography, and especially in the manufacture of medicine, where bromides and other derivatives of bromine are of considerable value. It is used as a mild oxidising agent and also as a disinfectant, it being for the latter purpose absorbed in kieselguhr (which takes up 75 per cent. of its weight of Br), and sold as "*Bromum solidification*" (German Patent, 21,644).

Bromide of Iron, Fe_3Br_8, is made at Stassfurt, serving as a raw material for the manufacture of sodium or potassium bromide. Steel wire and turnings are treated in a closed stone trough with Br vapour and steam at a temperature of 170° C. When the temperature falls to 100° the brown-red solution of Fe_3Br_8 is run off into transport barrels, where it is allowed to crystallise.

Bromine Salt, $NaBrO_3 + 2NaBr$, is made by saturating concentrated NaOH with Br, draining off the mother liquor from the resulting solid salt, and adding $NaBrO_3$ (electrolytically prepared) until the above composition is attained. The mixture is then ground and packed in kegs. It is used in the extraction of gold ores.

Potassium Bromide, KBr, is made (1) by running a concentrated solution of iron bromide (Fe_3Br_8, see above) into a hot concentrated solution of K_2CO_3, until the resulting liquid is almost neutral, or at most, faintly alkaline. 100 parts of iron bromide require 56·60 parts of potassium carbonate. Iron hydroxide is precipitated and KBr goes into solution. The liquid is boiled, filtered from the precipitated iron hydroxides, evaporated to dryness, lixiviated with sufficient water to take up the soluble KBr and leave undissolved the difficultly soluble K_2SO_4; concentrated to 1.53 sp. gr. at a boiling heat, then allowed to evaporate at a very gentle heat, when hard crystals of KBr separate. The crystals are washed and dried at 40°-50° C. (not above). Any chloride in the bromide cannot be easily removed, hence the necessity of employing chlorine-free bromine.

Formerly KBr was made by saturating KOH with Br, evaporating with a little charcoal to destroy any $KBrO_3$ formed ($6Br + 6KOH = 5KBr + KBrO_3 + 3H_2O$), then lixiviating with water and separating the KBr by crystallisation.

About 120 tons of KBr are made annually in Germany, and the same amount in U.S.A.

Properties.—White cubes, 100 parts H_2O, dissolve 62 parts KBr at 15° C. M.P. 750° C. Volatilises at higher temperatures.

Uses.—In photography and in medicine.

Statistics.—Bromine was first manufactured at Stassfurt in 1865. The following figures show the output:—1865, 1¼ tons; 1885, 260 tons.

Considerable quantities are also manufactured in America from the bromine-rich springs in **Ohio** and elsewhere:—1885, 120 tons; 1902, 230 tons.

CHAPTER VIII

The Iodine Industry

CHAPTER VIII

THE IODINE INDUSTRY

LITERATURE

GEOFFREY MARTIN and ERNEST DANCASTER.—"The Halogens," forming Vol. VIII. of "Modern Inorganic Chemistry." Edited by Newton Friend. 1915.

NEWTON.—*Journ. Soc. Chem. Ind.*, 1903, **22**, 469.

G. G. HENDERSON.—Article, "Iodine," in Thorpe's "Dict. Applied Chem." Vol. 3. 1912.

IODINE ($I = 126.92$) is a fairly widely distributed element, occurring, combined with metals, in small quantities in the soil, the sea, sea plants, and animals. Certain sea plants, especially the deep sea weed, *Fucus palmatus*, possess the power of storing up a considerable amount of iodine, and from these plants a portion of the iodine of to-day is obtained. The deep sea plants contain more iodine than shallow sea plants.

This is shown by the following table, which gives the percentage of iodine in the dried plant:—

		Per Cent.
Cut weed from shallow water	*Fucus filum*	0.0894
	,, *vesiculosus*	0.001 to 0.0297
	,, *serratus*	0.0856
	,, *ascophyl nodosum*	traces to 0.0572
Drift weed from deep water	*Laminaria digitata* (*stem*)	0.4535
	,, ,, (*frond*)	0.2946
	,, *stenophylla*	0.4777
	,, *saccharina*	0.23 to 0.2704

Consequently the manufacture of iodine from shallow water weed has been largely abandoned in favour of drift weed from deep water.

The bulk of the iodine of commerce, however, is now derived from crude Chile saltpetre or caliche, $NaNO_3$. The mother liquors remaining after the $NaNO_3$ has crystallised out contain 5-20 per cent. of sodium iodate, crude caliche containing 0.2 per cent. of iodine.

Manufacture of Iodine from Caliche.—The mother liquor remaining after the crystallisation of the sodium nitrate is treated with sodium bisulphite solution, and the iodine separates out in a solid form:—

$$2NaIO_3 + 5NaHSO_3 = 3NaHSO_4 + 2Na_2SO_4 + H_2O + I_2.$$

The solid iodine is settled, washed, pressed into blocks, and purified by sublimation in iron retorts, the vapours condensing in a series of earthenware receivers.

An account of the process is given by Newton (*Journ. Soc. Chem. Ind.*, 1903, **22**, 469), from whose paper the following details are taken:—

Sodium bisulphite is prepared by mixing together some 85 parts of impure sodium nitrate, 15 parts of fine coal, and water. The mixture is made into a conical mound, surrounded by a trench, and ignited. The crude sodium carbonate thus obtained is made into a saturated solution, settled in an iron tank, and then sulphur dioxide gas is blown through the liquid by means of a steam blower. The sulphur dioxide gas is made by burning native sulphur on an iron plate in a "sulphur furnace" (see Martin's "Industrial Chemistry," Vol. II., for modern sulphur burners), which consists simply of an iron oven with a flue passing from it to the cylindrical tank. The sulphur dioxide is passed into the crude sodium carbonate until it is all converted into sodium bisulphite. The bisulphite solution is then run into the *reservoir tanks*, which are placed a foot above the level of the large lead-lined (or pitch-coated) wooden "precipitation" tanks, which are about two-thirds filled with the final mother liquor obtained during the purification of the nitrate, and which contains all the sodium iodate. The bisulphite solution is next run into these "precipitation" tanks, the liquids being thoroughly stirred by means of wooden paddles or by air forced in through perforated pipes in the bottom of the tanks. Iodine is precipitated according to the foregoing equation. It is collected and removed, the last traces which remain after the bulk has been removed being collected by means of a calico bag at the end of a stick. The iodine is then water-washed, filter-pressed, and sublimed in iron retorts. These consist of horizontal cast-iron cylinders, tapering at one end to a conical form. The outlet, which is 6 in. in diameter, is connected to a series of eight or ten ordinary earthenware drain pipes (or aludells similar to those used in the manufacture of iodine from kelp) which are luted together by clay. Many different variations of this process have been suggested. Sometimes SO_2 gas is passed directly into the mother liquors, and any iodide, NaI, remaining is decomposed by adding chlorine water. Sometimes the iodide—especially in liquors very poor in this substance—is directly precipitated as cuprous iodide, Cu_2I_2, by adding $CuSO_4$ and $FeSO_4$, the Cu_2I_2 is then distilled with MnO_2 and H_2SO_4 and the I distilled over. Sometimes the Cu_2I_2 is heated with H_2SO_4 and ferric oxide (see German Patent, 209,501):—

$$Cu_2I_2 + 6H_2SO_4 + 2Fe_2O_3 = I_2 + 2CuSO_4 + 4FeSO_4 + 6H_2O.$$

Electrolytic Iodine.—Attempts have been made to prepare iodine electrolytically (see Rink, German Patent, 182,298) from the caliche mother liquors.

The anodic compartment contains as anode a carbon plate immersed in a concentrated NaCl (or halogen salt) solution. The cathode consists of an iron plate immersed in a slow-moving stream of the liquor to the electrolyser. Separating the anodic from the cathodic space is an asbestos cloth diaphragm. Under the influence of the electric current the iodine ions pass away from the cathodic space to the anode and are discharged into the concentrated solution of halogen salt, which possesses an extremely highly developed power of dissolving iodine. The anodic liquors with the iodine therein is run off from time to time and the iodine expelled therefrom. If no diaphragm is used for separating the anodic and cathodic spaces, a process analogous to the Bell process (see p. 21) is used, the less dense cathodic liquors being separated from the heavier anodic liquors by their specific gravity.

Parker and Robinson (English Patent, 11,479, 1888) place a solution of alkali iodides, acidified with sulphuric acid, in an electrolytic cell, which is divided into two compartments by a diaphragm, and provided with a carbon or platinum anode and an iron cathode. An electric current is sent through the fluid, and the iodine which is liberated at the anode is collected, washed, and dried.

Manufacture of Iodine from Seaweed.—The seaweed (chiefly *Laminaria digitata* and *L. stenophylla*) cast up in the spring after stormy weather on the coasts of France and Ireland, Scotland and Japan, is dried in the sun during the summer, and is then burnt in large heaps in shallow pits; the ash[1] may contain from 0.1 0.3 per cent. of iodine.

Since much iodine is lost by volatilisation during this burning process, Stanford, in 1862, subjected the weed to destructive distillation in closed retorts, the whole of the iodine remaining in the ash, while the tar and ammoniacal liquors were also recovered. However, the cost of plant and fuel rendered the process unremunerative.

Next the ash is lixiviated, and the iodine passes into solution as KI. The carbon remaining after the lixiviation of the ash resembles animal charcoal, and is used for similar purposes.

Several processes have been worked in which the plants are not carbonised at all. In one process the plants are stated to be simply directly lixiviated, the residual apparently unaltered plants being converted into "algin," a gelatinous substance used as a substitute for isinglass, bladder skins, etc. In another process the plants are heated with dilute sulphuric acid or other acid; here, again, previous carbonisation is avoided, and the residue of seaweed is utilised as manure. Stanford heated the weed with Na_2CO_3.

There results from the lixiviation (which is systematically carried out) a concentrated solution of alkali carbonates, sulphates, chlorides, sulphites (traces)

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[1] According to Ernest A. Dancaster, in this country the term **kelp** is applied to both the weed and the ash, although the latter is also known as **kelp ash**. In France the term **varech** is applied to all seaweed (the word being allied to our word **wrack**), and the burnt ashes are known as **condres de varech**.

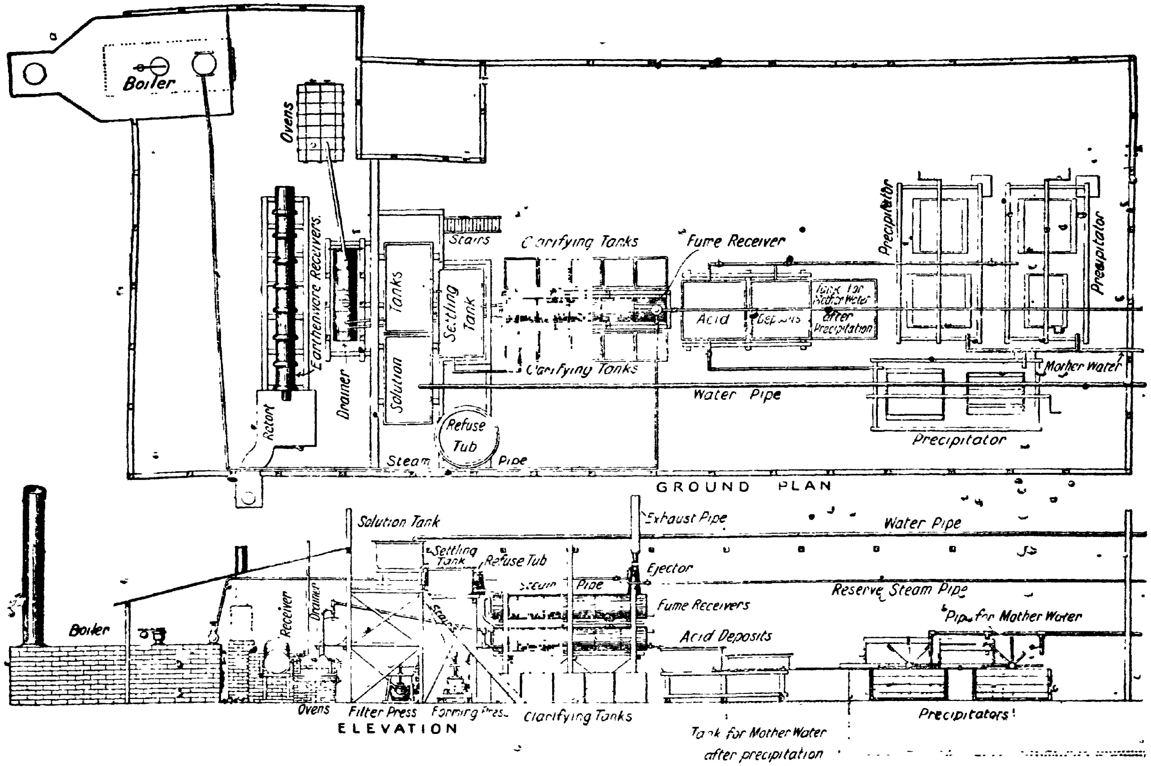

Boiler
Ovens
Earthenware Receivers.
Retort
Drainer
Tanks
Solution
Settling Tank
Stairs
Clarifying Tanks
Fume Receiver
Clarifying Tanks
Refuse Tub
Steam Pipe
Acid Deposits
Tank for Mother Water after Precipitation
Precipitator
Precipitator
Mother Water
Water Pipe
Precipitator
GROUND PLAN
Solution Tank
Settling Tank
Refuse Tub
Exhaust Pipe
Water Pipe
Ejector
Steam Pipe
Reserve Steam Pipe
Fume Receivers
Pipe for Mother Water
Acid Deposits
Boiler
Receiver
Drainer
Stairs
Ovens
Filter Press
Forming Press
Clarifying Tanks
Precipitators
Tank for Mother Water after precipitation
ELEVATION

Fig. 40.—Plant for Manufacturing Iodine from Caliche.

(Taken, by kind permission, from Thorpe's "Dictionary of Applied Chemistry." Published by Longmans & Co.)

sulphides (traces), bromides, and iodides of the alkali metals. The solution is evaporated, and the chlorides, carbonates, and sulphates allowed to crystallise out. The mother liquors then contain the bromides and iodides. This liquor is then worked for iodine by the following processes:—

(1) Excess of H_2SO_4 is added to decompose sulphites and sulphide, and after removing any separated crystals, the liquid is run into a hemispherical iron boiler mounted in brickwork over a fire, and fitted with a leaden hood provided with a still head (Fig. 41). Manganese dioxide is thrown in, and when the temperature reaches about 60° C. iodine is evolved, and, escaping through the still head, condenses in a series of glass or earthenware receivers termed "udells." The joints of the apparatus are luted gas-tight by clay. The iodine distilling over condenses in the earthenware or glass condensers or "udells." When no more iodine comes over, the stills are connected with another set of receivers and Woulff's bottles, and more manganese dioxide is added. Bromine is evolved, and is thus collected separately from the iodine. The equation representing the change is thus:—

$$MnO_2 + 2NaI + 3H_2SO_4 = I_2 + 2NaHSO_4 + MnSO_4 + 2H_2O.$$
$$MnO_2 + 2NaBr + 3H_2SO_4 = Br_2 + 2NaHSO_4 + MnSO_4 + 2H_2O.$$

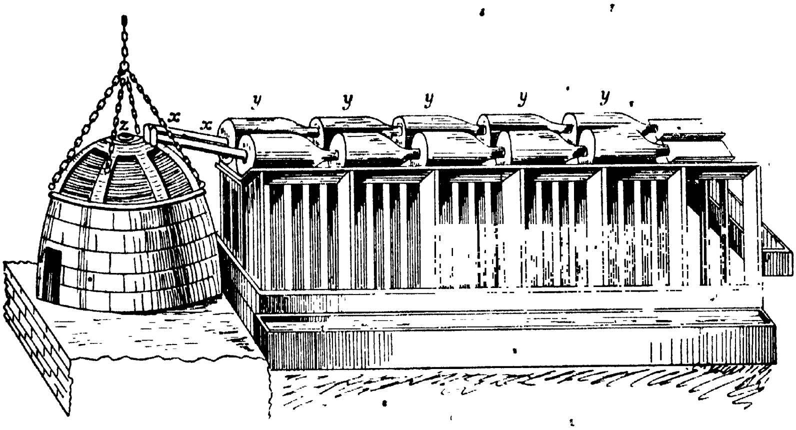


Fig. 41.—Iodine Still.

The iodine thus obtained is impure, containing chloride, bromide, and cyanide of iodine. It is purified by sublimation as above described.

(2) Other processes are to heat the liquor with sulphuric acid and ferric chloride, $FeCl_3$, with sulphuric acid and nitric acid, sulphuric acid and chlorate, or bichromate, etc. All the oxidising agents liberate the iodine from the liquid. Sometimes the calculated amount of Cl gas is led into the liquid when iodine is precipitated. However, the chlorine must not be in excess, or iodine chloride would be formed.

When the liquid is very poor in iodine, it may be precipitated as cuprous iodide, Cu_2I_2, by adding ferrous sulphate and copper sulphate to the liquid. From the Cu_2I_2 the iodine can then be liberated by heating with sulphuric acid and manganese dioxide.

(3) Occasionally a process of extraction with organic solvents is resorted to. Thus, after liberating the iodine by adding sulphuric and nitric acid, the liquid is agitated with petroleum naphtha or benzol, when the iodine dissolves, and the petroleum or benzol layer of iodine is then separated from the aqueous layer, and shaken up with an aqueous caustic soda, whereby the iodine is fixed as iodide or

iodate of sodium, and so is withdrawn from the hydrocarbon. The petroleum or benzol is drawn off, and the iodine is then liberated by HCl thus:—

$$5NaI + NaIO_3 + 6HCl = 6NaCl + 3H_2O + 3I_2.$$

More recently, instead of using a volatile solvent, the use of vaseline oil (the heavy oil from Galician petroleum) has been used for extracting the iodine. The liquor containing the iodine is treated with vaseline oil in such a manner that those portions of the liquor from which the bulk of the iodine has already been extracted are treated with fresh vaseline oil, which takes up all the iodine out of the liquor. Also those portions of the vaseline enriched in iodine come only into contact with the iodine-rich liquors. In this way efficient extraction is secured.

Next the oil is distilled with steam; the iodine coming over, the oil is left behind and used again.

In general, one ton of carbonised seaweed yields 10-12 lbs. of iodine.

Iodine from Phosphates.—Thiercelin (*Bull. Soc. Chem.*, 1874 (2), **22**, 435) places a mixture of equal quantities of iodine-rich phosphate, sulphuric acid, and water in a vat, and keeps the mass well stirred. The iodine is liberated and passes over into a condensing chamber.

Purification.—Commercial iodine always contains traces of chlorine and bromine, either chemically combined or in solid solution. The purification is best effected by dissolving the resublimed iodine in a concentrated solution of KI, when it dissolves to a dark solution, possibly containing the compound KI_3. On adding excess of water the iodine is precipitated, and is washed and dried. The dry iodine is then mixed with solid KI and slowly sublimed. The sublimate consists of practically pure iodine. Pure iodide can also be obtained by heating cuprous iodide, Cu_2I_2, to about 240° C. in a stream of air.

Properties.—Pure iodine is a dark bluish-black, lustrous, crystalline solid. Atomic weight of I = 126.92; M.P., 116.1° C.; B.P., 184.35°; specific gravity of solid, 4.933 at 4° C.; vaporises slowly; very sparingly soluble in cold water. 100 vols. of a saturated solution at 25° C. contains only 0.32 g. of iodine. At 15° C. 1 part iodine dissolves in 3,750 parts of water, and in 2,200 at 30°. It is much more soluble in a concentration solution of KI (where it possibly forms the component KI_3), and also in alcohol, ether, acetone, chloroform, benzene, carbon disulphides, and other organic solvents. The tincture of iodine of the *Pharmacopœia* contains ½ oz. iodine, ¼ oz. KI, and 1 pint of rectified spirits. Potash or soda at once decolorises a solution of iodine, forming potassium iodide and iodate, thus:—

$$3I_2 + 6KHO = 5KI + KIO_3 + 3H_2O.$$

With concentrated HNO_3 iodine is oxidised to iodic acid, HIO_3.

Test.—Iodine produces a splendid blue colour with starch paste. The blue colour disappears on warming the solution, but reappears on cooling.

Alkali Iodides.—(1) In order to produce potassium iodide, KI (or sodium iodide, NaI), the usual process is to add iodine in small portions to hot KOH (or NaOH) and evaporate. A mixture of potassium iodide, KI, and potassium iodate, KIO_3, is obtained (NaI or $NaIO_3$ if NaOH is used). The mixture is next mixed with carbon and ignited, which decomposes all iodate, and the iodide is then extracted with cold water and crystallised out. Improvements on this method of manufacture are suggested in the German Patent, 138,008.

(2) In another process the formation of iodate is prevented by allowing iodine to act on alkali in the presence of a reducing substance such as potassium thiosulphate. The following change occurs:—

$$K_2S_2O_3 + 10KOH + 8I = 8KI + 2K_2SO_4 + 5H_2O.$$

Sometimes sodium carbonate is used:—

$$Na_2S_2O_3 + 5Na_2CO_3 + 8I = 8NaI + 2Na_2SO_4 + 5CO_2.$$

On evaporating, the K_2SO_4 or Na_2SO_4 is easily separated by crystallisation from the much more soluble iodides.

Statistics relating to Iodine.—Most of the iodine at present produced comes from the mother liquors of the sodium nitrate (caliche) works of South America:—

1879	77.35 tons	1904	458.21 tons
1881	200.06 ,,	1905	564.20 ,,
1890	419.74 ,,	1906	351.20 ,,
1900	306.13 ,,		

Chile alone exported in 1904, 9,961 Spanish cwt.

The amount of iodine produced from seaweed is small, being principally worked in France, Norway, and England. However, in recent years Japan has begun to make large quantities of iodine from seaweed, and if the U.S.A. seriously attempt the recovery of potash from seaweed on the Pacific coast on a large scale, an important additional source will be added to those existing. The following figures give the Japanese export of KI (potassium iodide) in kin (1 kin = 1.3 lbs.):—

1902	1903	1904
3,051.	22,371.	52,012.

The following statistics relate to the German import and export of iodine:—

Year.	Total Import.		Imported from		
	Quantity in Tons.	Value in Million Marks.	Great Britain.	Japan.	Chile.
1890	138	3.7	77	...	41
1900	236	5.4	110	6	100
1904	270	6.0	50	20	170
1905	377	12.8	60	20	200
1906	297	5.8	...	...	...
1907	147	2.65	27	17	76
1908	194	3.5	55	...	112

The German export of **iodine** in 1901 was 30 tons. In 1907 it rose to 44 tons.

Germany exports large amounts of finished iodine products, fine chemicals containing iodine, as shown by the following figures:—

GERMAN EXPORT OF IODINE PREPARATIONS

Year.	Total Import.	
	Quantity in Tons.	Value in Million Marks.
1890	106	2.9
1900	138	3.0
1904	170	4.2
1905	170	5.3
1907	145	2 5

CHAPTER IX

The Hydrofluoric Acid Industry

CHAPTER IX

THE HYDROFLUORIC ACID INDUSTRY

LITERATURE

GEOFFREY MARTIN and E. DANCASTER.—"The Halogens," forming Vol. VIII. of "Modern Inorganic Chemistry." Edited by Newton Friend. 1915.

A. G. BETTS.—*Eng. and Min. Journ.*, 1907, p. 153.

ZELLNER.—"Die kunstlichen Kohlen." Berlin, 1903.

AQUEOUS hydrofluoric acid, HF, is usually obtained by heating calcium fluoride, CaF_2, with concentrated sulphuric acid:—$CaF_2 + H_2SO_4 = CaSO_4 + 2HF$. In recent years the technical importance of hydrofluoric acid has considerably increased, as it is used on a fairly large scale for the purification of artificial carbon and graphite, in dyeing, in etching glass, in the brewery, etc., and consequently considerable improvements have been effected in the apparatus for preparing this substance. Many factories which prepare acids for use in chemical industry have their own special plant for producing hydrofluoric acid.

Manufacture.—Fig. 42 shows a small scale apparatus for preparing aqueous HF. A leaden retort A, on which a leaden head B is cemented, has placed within it a mixture of calcium fluoride and oil of vitriol. On heating the gaseous mixture HF is evolved and passes into a leaden receiver C, which contains a vessel of water D, best made of platinum, in which the HF condenses. The tube *g* serves as air and gas exit.

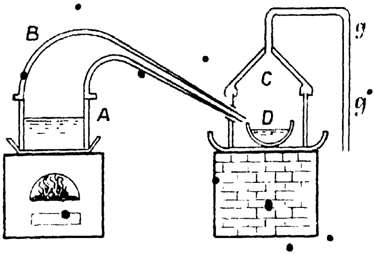


FIG. 42.—Small Still for Hydrofluoric Acid.

On a large scale, however, it is usual to use iron stills. Fig. 43 shows a large scale plant, working according to the Eckelt vacuum process.

a is a semispherical cast-iron pan, some 2 m. in diameter, and some 3.5 cm. to 4.5 cm. thick. This serves as the HF generator. On this stout pan rests a hemispherical leaden lid *b*. The lead of the semispherical lid is held rigid by being soldered over a framework of iron bands, which run together to a ring at the top, to which is fastened a ring *d* which serves to lift the lid when necessary. The lid is 1 cm. thick, and has at the base a broad 12 cm. flange, which fits exactly over the similar flange belonging to the iron pan beneath, and which forms an air-tight joint, the two flanges being securely clamped together by strong screw clamps.

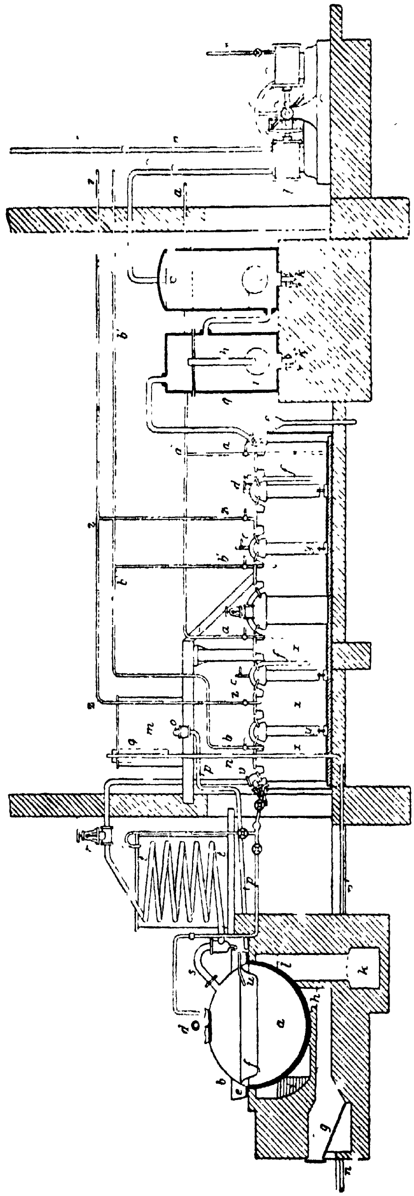


FIG. 45.—Plant for the Manufacture of Hydrofluoric Acid.

The thin lead sheet is turned up on the edge *e*, so as to form a sort of trough, which is kept filled with running cold water, which serves as a condensing arrangement and keeps the leaden cover from becoming too hot.

The heat of the furnace beneath might otherwise overheat the lead and cause it to melt. The cooling water flows in and out through special funnels.

Inside the lid is a protecting sheet of lead which runs round the periphery of the inside of the lid, and projects over the iron pan.

It serves to protect the latter from the cold dilute sulphuric acid, which keeps condensing on the leaden lid, and would otherwise run down the cast-iron surface of the lower pan, and rapidly corrode it.

The cast-iron pan is set in brickwork in such a manner that it is protected from the direct action of the flames. The hot gases come into contact with the metal at the opening *h*, and in order to prevent the cast-iron pan burning away locally at *h*, the whole cast-iron pan *a* is turned through an angle of 60° after every second charge, by means of iron hand grips attached to the iron pan. The tendency to burn is fairly pronounced, because towards the end of the operation solid crusts of calcium sulphate separate. Some 800-900 kg. of fluorspar is placed in the iron pan ***a***, then some 1,200-1,300 kg. of concentrated sulphuric acid is run out of a lead-lined tank (using compressed air to expel the acid) *m* into the iron pan ***a***. The HF vapours escape up the leaden tubes *s* and *t*, any sulphuric acid simultaneously carried over with the gas being condensed in the coil *t*, which is immersed in a tank of running cold water, and flows back again through the tube *u* into the pan *a*. The HF gas escapes and passes into the leaden vessels *x*,*x*,*x*, which are filled with water and connected together at the bottom in two sets of three by means of the tubes *y*,*y*. Each set of three vessels is placed in a tank filled with a running stream of cold water, being immersed right to the base of their necks. In the first two of each set of three the tubes do not dip below the surface of the water, so that the absorption of gas in the water takes place at the surface only. In the last vessel, however, the entry tube *t* dips into the water, so that the gas has to pass through the water before issuing out into the vacuum apparatus. This provision is necessary in order to avoid the necessity for using a very high vacuum to work the condensing arrangement. The acid gases escaping finally from the last vessel *x* are led into absorption towers (each about 2 m. high by 1 m. diameter), of which the first contains milk of lime or caustic soda solution, and the second is filled with dry slaked lime, placed on wooden gratings. The inside of each tower is well tarred to make it acid-resisting.

The gases then pass out, free from all acid fumes, into the cylinder *l*, whence by means of the vacuum pump they are forced out into the air through a long tube *n*. In general, to every set of absorption vessels there are two hydrofluoric acid generating stills employed, the absorption being regulated by the valve at *r*. It takes about forty-eight hours to work off a charge.

Bett (see *Engineering and Mining Journal*, 1907, p. 153) describes another process which is in use in various parts of the world. Shallow cast-iron pans are provided with lids, which are hermetically sealed by means of concentrated sulphuric acid. All the condensers, etc., which consist of leaden vessels, stand totally immersed in water. The charge is 1,000 kg. of ground fluorspar to 1,000-1,200 kg. concentrated sulphuric acid (66° Bé.).

All these methods suffer from the defect that a crust of calcium sulphate sets on the bottom of the decomposing pans, causing great difficulties. Several efforts have been made to overcome these defects. The proposal of L. Meyer (German Patent, 142,931, 1900) deserves mention. The retort is fixed in a furnace, and the decomposing pan consists of an iron trolley, running on wheels, which can be moved in or out of the furnace as desired. The fluorspar and sulphuric acid are mixed cold to a syrupy mass in this trolley, which is then run into the retort, the door shut, and the distillation carried out in the usual way. When the distillation is finished, the door is opened, and the trolley run out, while another similar trolley, freshly charged, is run in again. So that neither time nor heat is lost between the separate charges. A similar apparatus for making acetone is described in Martin's "Industrial Chemistry," Vol. I., German Patent, 134,977.

Sodium or potassium bisulphate ($NaHSO_4$) or ($KHSO_4$) may be used instead of sulphuric acid in decomposing CaF_2 (see German Patent, 116,848).

Purification.—Technical hydrofluoric acid solution invariably contains hydrofluorsilicic acid, H_2SiF_6, derived from the silica, SiO_2, almost invariably present in the commercial fluorspar, CaF_2, used. It usually contains, as well, some H_2SO_4, HCl, SO_2, As, Fe, Pb, Ca, etc., derived from impurities in the materials used in the manufacture.

K. F. Stahl (*Zeit. angew. Chem.*, 1896, **9**, 225; *Journ. Amer. Chem. Soc.*, **18**, 415) gives the composition of the commercial acid as follows:—

HF	39.6-54.2 per cent.
H_2SiF_6	2.7-14.9 ,,
H_2SO_4	0.8-4.0 ,,

By repeated distillation an acid of constant composition and boiling point may be attained (at 75° min. and 111° C. B.P. the acid contains HF = 43.2 per cent., $D^{18} = 1.138$ according to Deussen, *Zeit. anorg. Chem*, 1906, **49**, 207), but the pure acid can only be obtained by special chemical treatment, as with distillation the H_2SiF_6 simply goes over with the acid.

Gore (*Phil. Trans.*, **1869**, 173; *Journ. Chem. Soc.*, [2], **7** (1869), 368) purifies commercial by diluting the technical acid until it contains less than 40 per cent. HF (with more than this H_2S will not precipitate lead), passes in excess of H_2S (to precipitate the Pb, As, etc.), adds more than enough of K_2CO_3 to combine with all the H_2SiF_6 and H_2SO_4 present (which precipitates most of the H_2SiF_6 as K_2SiF_6, decants the liquid, removes any H_2S present, by adding Ag_2O or AgF or Ag_2O, and then distils from a leaden retort, leading the vapour through a platinum condenser into water contained in a platinum basin.

The pure acid must not come into contact with Pb. Thorpe and Hambly (*Journ. Chem. Soc.*, 1889, **55**, 163) treat with $KMnO_4$, then convert the acid into KF.HF by adding KF, and then dry this compound and decompose it by heating in a platinum retort:—

$$KF.HF = KF + HF.$$

See also Moissan (*Ann. Chim. Phys.*, [6], **24** (1891), 224). The pure acid is now invariably prepared by heating the salt KF.HF.

Properties.—The aqueous acid is a highly corrosive, dangerous liquid, contact of the vapour with the eyes and skin being highly dangerous. The acid, and some of its salts (*e.g.*, NH_4F), are principally used for etching glass, acting on the SiO_2 of glass as follows:—

$$4HF + SiO_2 = 2H_2O + SiF_4.$$

The SiF_4 escapes as a gas. It is acted on by water thus:—

$$3SiF_4 + 3H_2O = H_2SiO_3 + 2H_2SiF_6.$$

According to W. Winteler (*Zeit. angew. Chem.*, **15**, 33, 1902) the density of the aqueous acid at 20° C. is given by the following table:—

Per Cent. HF.	Sp. Gr.	° Bé.	Per Cent. HF.	Sp. Gr.	° Bé.
1	1.003	0.5	26	1.092	12.0
2	1.007	1.0	27	1.095	12.4
3	1.011	1.5	28	1.098	12.7
4	1.014	2.0	29	1.101	13.1
5	1.018	2.5	30	1.104	13.4
6	1.023	3.0	31	1.106	13.7
7	1.027	3.5	32	1.109	14.1
8	1.030	4.0	33	1.112	14.4
9	1.035	4.5	34	1.114	14.7
10	1.038	5.0	35	1.117	15.0
11	1.041	5.5	36	1.120	15.4
12	1.045	6.0	37	1.122	15.7
13	1.049	6.5	38	1.25	16.0
14	1.052	7.0	39	1.27	16.3
15	1.055	7.5	40	1.130	16.5
16	1.059	8.0	41	1.133	16.8
17	1.062	8.4	42	1.136	17.2
18	1.066	8.8	43	1.138	17.5
19	1.069	9.3	44	1.141	17.8
20	1.072	9.7	45	1.143	18.1
21	1.076	10.1	46	1.146	18.4
22	1.079	10.5	47	1.149	18.7
23	1.082	10.9	48	1.152	19.0
24	1.086	11.3	49	1.154	19.3
25	1.980	11.7	50	1.157	19.5

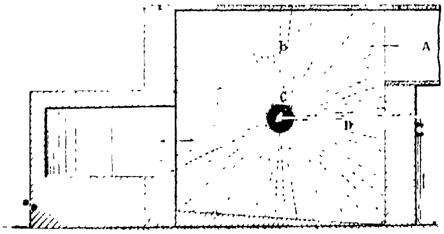
Eckelt (*Chem. Zeit.*, 1898, **22**, 225) gives another table which differs in some respects from that given. The density of aqueous HF may be determined by using an ebonite pyknometer with ends which screw off and on (see Zellner, *Monatsh.*, **18**, 749, 1897). With acids which are not very strong, a simple metal floating hydrometer may be used, the metallic surface being painted over with a hard pitch.

Storage and Transport.—Large quantities of the aqueous acid may be transported in vessels of lead (see Stahl, *Zeit. angew. Chem.*, 1896, **9**, 225, and also Eckelt, *Chem. Zeit.*, 1892, **16**, 17). It may also be transported in cast-iron vessels, or glass vessels coated internally with guttapercha, bakelite, etc. Small quantities are usually kept in indiarubber, ebonite, or guttapercha bottles (see Bendikt, *Chem. Zeit.*, 1891, **15**, 881). Flasks made of paraffin wax or ceresin are also suitable.

Uses.—Formerly HF was used almost solely for glass etching. The glass is covered with a layer of wax, the portions to be etched being uncovered by removing the wax with a sharp instrument. The acid, when applied (either as vapour by gently warming, or else in an aqueous solution), leaves a sharp mark. Ammonium fluoride in HF solution is also used for dull etching glass.

More recently, however, the importance of HF has greatly increased owing to its use in other directions; *e.g.*, considerable quantities are used for purifying artificial graphite from SiO_2, etc. (see Zellner, "Die Künstliche Kohlen," Berlin, 1903). In dyeing double fluorides of antimony are widely used as a substitute for tartar emetic. In the spirit and brewing industry HF is used extensively on account of its antiseptic effect, yeast being not nearly so sensitive to the acid as other organisms, and so the fermentation proceeds more uniformly when HF is used (see Martin's "Industrial Chemistry," Vol. I., **Organic**; also Effront, *Bull. Soc. Chem.*, 1890, [3], 4, 337). Stahl (*Zeit. angew. Chem*, 1896, 9, 225) recommends the use of a 1-2 per cent. HF solution to open out petroleum bores, and also for cleaning iron castings from sand (SiO_2), and also for cleaning copper articles

Dilute aqueous HF has been used for removing the weighting matters from silk (see *Zeit. f. Farben und Texilchemie*, 1903, **2**, 160, 210, 261; Gnehm and Dürsteler, *Farberei. Zeit.*, 1906, **17**, 217; Ristenpart, **18** (1907), 273)



Ground Plan.

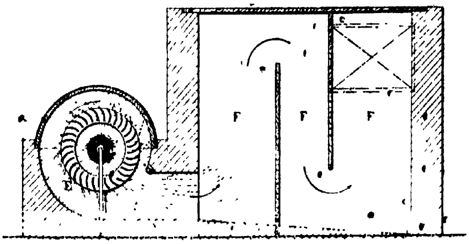
FIG. 44.—Superphosphate Den.

Hydrofluorsilicic Acid, H_2SiF_6.—This acid is obtained by leading silica tetrafluoride, SiF_4 (which is evolved by allowing silica to act on HF:—$SiO_2 + 4HF = SiF_4 + 2H_2O$), into water:- $3SiF_4 + 4H_2O = H_4SiO_4 + 2H_2SiF_6$. Gelatinous silicic acid is simultaneously produced. H_2SiF_6 is thus produced whenever the gases evolved by treating material containing fluorides with siliceous materials and concentrated sulphuric acid are led into water. Thus large quantities of H_2SiF_6 and its salts are obtained as by-products in the **superphosphate** industry (see Martin's "Industrial Chemistry," Vol. II., under **Manures**). Natural and artificial phosphates, often containing considerable amounts of fluorides and siliceous matter, are in this industry treated with concentrated sulphuric acid in order to produce the phosphate in a soluble form, suitable for manuring purposes. The gases thus evolved in the furnaces (which contain SiF_4, free HF, H_2O, CO_2, etc.) are sucked out and are led into large condensing "dens" or chambers (of 100 cub. m. capacity), best built of pitchpine and provided with a number of dividing walls, against which the gases impinge. The steam and SiF_4 here condense and react according to the equations:—

$$3SiF_4 + 4H_2O = 2H_2SiF_6 + H_4SiO_4;\ SiF_4 + 3H_2O = 4HF + H_2SiO_3;\ 2HF + SiF_4 = H_2SiF_6.$$

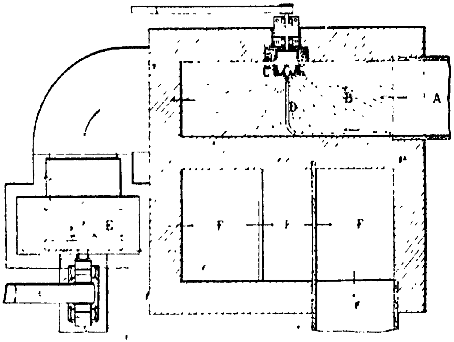
The gases not absorbed in the first chamber pass out into another similar absorption chamber, in which the gases come into contact with a spray of *cold* water (steam does not react so well with SiF_4), and the gases not absorbed here escape by means of a tall chimney into the air.

A more efficient system of absorbing the SiF_4 containing gas is that devised by Paul Kestner, Düsseldorf (see Figs. 44, 45, and 46). The gases from the pan wherein the phosphate is treated with H_2SO_4 pass by means of the pipe A into the space B. This contains a rapidly rotating "centrifugal atomiser" C, which fills the whole chamber with a fine spray or mist of water particles. This cools and partially absorbs the entering gases, which then pass on through the "turbo-atomiser" E. This consists of a fan-wheel E, which is built up of small blades after the manner of a turbine. In the centre of this fan is a rotating "atomiser" which ejects a fine spray of water through the rapidly rotating blades of the surrounding fan wheel E, and thus causes the gas coming from the chamber B to be so thoroughly churned up and mixed with water that complete absorption of the acid components follow, the escaping gases passing away quite free from acid fumes through a chamber F provided with baffles, and so out to the chimney. The water, falling as drops, flows away from F in the form of a solution of fluorsilicic acid, the liquors containing gelatinous silicic acid in suspension. The liquid is passed through a filter press and then stirred up with NaCl solution, when there separates out a white gelatinous precipitate of sodium silicofluoride, Na_2SiF_6, which is produced thus:—



Elevation.

FIG. 45.—Superphosphate Den.



Ground Plan.

FIG. 46.—Superphosphate Den.

$$2NaCl + H_2SiF_6 = Na_2SiF_6 + 2HCl.$$

This Na_2SiF_6, when washed over with cold H_2O, dried, and passed through a sieve, contains $Na_2SiF_6 = 98.6$ per cent, $NaCl = 0.72$, $SiO_2 = 0.54$, $H_2O = 0.14$.

It is sold to enamelling works, and finds some application in the manufacture of "milk" glass.

H_2SiF_6 is also obtained as a by-product when earthenware vessels are treated with HF in order to increase their porosity, high tension steam being afterwards blown through them (see Prior, *Zeit. angew. Chem.*, **1903**, 195), or when graphite is treated with HF (to free it from SiO_2). See also German Patent, 105,734 (1898). The German Patent, 116,848, describes a process for manufacturing the acid.

Properties.—H_2SiF_6 is a strong acid: it attacks the skin. When concentrated it is hygroscopic, and attracts moisture from the air until a certain definite concentration is attained. The acid, when boiled or evaporated, volatilises without a residue.

Uses.—The acid now finds considerable application as a disinfectant, for deliming skins in tanning (Martin's "Industrial Chemistry," Vol. I.), and in the electrolytic precipitation of lead. Its sodium salt is used (see above) in enamelling and in the manufacture of "milk" glass. Fluorsilicates (fluates) are now used as a hardening agent of certain cements used in building (Martin's "Industrial Chemistry," Vol. II., "Artificial Stone").

CHAPTER X

Peroxides and Peracids

CHAPTER X

PEROXIDES AND PERACIDS

BY G. W. CLOUGH, D.Sc.

I.—PEROXIDES

A PEROXIDE is an oxide containing more oxygen, combined with a certain weight of an element, than is contained in the highest basic or acidic oxide of the element. The true peroxides, or **superoxides** as they are frequently called, differ from the "false" peroxides or **polyoxides** in that they yield hydrogen peroxide as a product on treatment with excess of water or a dilute acid. Since hydrogen peroxide possesses acid properties in aqueous solution, the superoxides may be regarded as salts of hydrogen peroxide. In consequence of the ease with which they are converted into the parent substance, they find wide application as oxidising, bleaching, and disinfecting agents.

Sodium Peroxide, Na_2O_2, is manufactured by passing a current of air, carefully freed from moisture and carbon dioxide, over slices of sodium resting on aluminium trays which pass through a tubular iron vessel. The temperature is maintained at about 300°. The oxidation is effected slowly by applying the principle of counter currents; the fresh sodium comes into contact with air poorest in oxygen, whereas the fresh air first passes over the almost completely oxidised material (German Patents, 67,094 and 95,063). The hydrate, $Na_2O_2.8H_2O$, is prepared by mixing sodium peroxide with six to eight times its weight of powdered ice or snow.

Properties.—Commercial sodium peroxide is a pale yellow powder containing 92-98 per cent. Na_2O_2. It is exceedingly soluble in water, which at the ordinary temperature decomposes it, yielding sodium hydroxide and oxygen. Although sodium peroxide only evolves oxygen at a high temperature, it is a vigorous oxidising agent, usually causing organic materials to burst into flame. An aqueous solution ($\frac{1}{2}$ per cent.) is employed for bleaching textile fabrics, but in the case of animal fibres (silk and wool) the soda formed must be neutralised with dilute sulphuric acid. Sodium peroxide is a constituent of some washing powders. "**Oxone**" is compressed sodium peroxide, and "**Oxylith**," which evolves oxygen on treatment with water, is a compressed mixture of sodium peroxide and bleaching powder.

The amount of active oxygen in sodium peroxide may be ascertained by treating 1 g. of the sample with 15 c.c. water and 2 drops of concentrated cobalt chloride solution, and measuring the oxygen evolved (Archbutt, *Analyst*, **20**, 3).

Barium Peroxide, BaO_2, is manufactured by passing air, freed from carbon dioxide and moisture, over barium monoxide, BaO, heated uniformly in retorts at 500°-600°. The success of the operation depends on the monoxide being in a porous condition. Several methods are in use for the preparation of the monoxide in a suitable physical state for conversion into peroxide. It may be produced (1) by heating barium nitrate (German Patent, 128,500); (2) by heating at a high temperature an intimate mixture of witherite and carbon free from hydrogen (German Patent, 149,803); (3) by heating barium carbonate or barium hydroxide with barium carbide in the absence of air (German Patents, 135,330 and 142,051);

or (4) by heating in an electric furnace barium sulphate (4 mols.) with carbon (5 atoms) in the form of coke (United Barium Co., of Niagara Falls).

In order to obtain pure barium peroxide from the commercial product, the latter is rubbed into a paste with water and is stirred into well-cooled dilute hydrochloric acid. To the resulting turbid liquid baryta is added until the precipitation of silica and metallic oxides is complete. After filtration, excess of baryta is added, when pure hydrated barium peroxide, $BaO_2.8H_2O$, is precipitated, and subsequently filtered, washed, and dried.

Properties.—Technical barium peroxide is a grey mass, whereas the pure compound is a white powder. At 700° it evolves oxygen yielding the monoxide. Barium peroxide is used for the manufacture of hydrogen peroxide, as a bleaching agent, and mixed with paraformaldehyde as a disinfectant. It is also employed for removing organic impurities from sulphuric acid, and as an addition to lithophone for preventing that pigment from becoming grey in sunlight (German Patent, 163,455).

Calcium Peroxide, CaO_2, cannot be prepared by heating quicklime in air. Hydrated calcium peroxide is precipitated in the form of fine needles when aqueous hydrogen peroxide is added to lime water. It is also prepared by adding a compressed mixture of sodium peroxide and slaked lime in molecular proportions to iced water (German Patents, 128,617 and 132,706). According to American Patent, 847,670, aqueous calcium chloride may be mixed with hydrogen peroxide, and the calcium peroxide precipitated by the addition of concentrated ammonia.

Properties.—Hydrates containing 8, 4, and 2 molecules of water are said to exist. The usual product contains $4H_2O$, and is a yellow crystalline powder, sparingly soluble in water, yielding an alkaline solution. Calcium peroxide is used as a bleaching agent, and is a component of some tooth powders. It may be employed with sulphuric acid for bleaching cotton seed oil, and for removing rancidity from oil.

Magnesium Peroxide, MgO_2, may be obtained by decomposing magnesium sulphate with sodium peroxide. A very antiseptic and stable product is produced by adding water to a mixture of sodium peroxide and magnesium hydroxide (or basic carbonate) (German Patent, 107,231). If sodium peroxide and alcohol are successively added to aqueous magnesium chloride at 20°, a powder containing 27 per cent. MgO_2 is precipitated, whereas if the precipitation occurs at a very low temperature (in a freezing mixture of sal ammoniac and ice) a product containing nearly 40 per cent. MgO_2 is obtained (English Patent, 2,743, 1902). Merck prepares "**magnesiumperhydrol**" by treating anhydrous magnesium oxide with chemically pure hydrogen peroxide; the product contains 15-25 per cent. MgO_2 (German Patent, 171,372).

Properties.—Magnesium peroxide is a white amorphous powder which is only sparingly soluble in water. It finds application as a bleaching agent and as an antiseptic (for wounds and skin diseases in the form of ointment).

Zinc Peroxide, ZnO_2, is produced when aqueous solutions of zinc salts are decomposed with sodium peroxide, the product having a variable composition ($ZnO_2 + ZnO$). Merck treats anhydrous zinc oxide with hydrogen peroxide; the product, "Zinc perhydrol," contains about 50 per cent. ZnO_2 (German Patent, 171,372). For other methods of preparation see German Patents, 141,821 and 151,129.

Properties.—Zinc peroxide is a white or very pale yellow powder. It is used as an antiseptic (both in the form of powder and ointment), and is also serviceable for arresting bleeding.

Hydrogen Peroxide, H_2O_2, is usually prepared from the cheaper peroxide, barium peroxide. The barium peroxide, finely powdered, is added gradually to a suitable dilute acid, *e.g.*, hydrochloric acid. In this case the barium in solution is subsequently precipitated with sodium sulphate, so that after filtration a solution containing hydrogen peroxide and sodium chloride is obtained. If dilute sulphuric acid is employed instead of hydrochloric acid, after filtering off the insoluble barium sulphate, an aqueous solution of hydrogen peroxide is obtained, containing, however, some impurities derived from the barium peroxide. Phosphoric acid is also frequently used for decomposing the barium peroxide. Well washed carbon dioxide may be passed through cooled water in which finely powdered barium peroxide is suspended (Merck, German Patent, 179,771); the insoluble barium carbonate is separated by filtration.

In order to obtain a pure aqueous solution of hydrogen peroxide, the pure hydrated barium peroxide is prepared as previously described (see **Barium Peroxide**). The moist product is added gradually with constant stirring to dilute sulphuric acid (1 : 5) maintained below 10° by the addition of ice. When the acid is neutralised, the mixture is stirred for some hours, allowed to settle and filtered. The usual concentration of hydrogen peroxide is 3 per cent. by weight.

A concentrated solution of hydrogen peroxide may be prepared by adding sodium peroxide to well cooled dilute sulphuric acid (20 per cent. calculated amount). On standing, about two thirds of the sodium sulphate crystallises and is separated by filtration. The filtrate is distilled under diminished pressure (Merck). Merck's "**perhydrol**"—the so-called 100 per cent. hydrogen peroxide—contains 30 per cent. H_2O_2, one volume of the solution yielding 100 volumes of oxygen. If a concentrated solution of hydrogen peroxide be distilled under diminished pressure, water distils over first, and subsequently nearly pure hydrogen peroxide (96 per cent.) distils over; boiling point, 84-85°/68 mm. or 69°/26 mm. Staedel found that on cooling the 96 per cent. product by ether and liquid carbon dioxide (−80°), crystallisation occurred, and when a nucleus of this product was introduced into the 96 per cent. liquid, pure transparent crystals of hydrogen peroxide, M.P. 2°, separated.

Hydrogen peroxide may also be manufactured by the hydrolysis of permono sulphuric acid in the presence of sulphuric acid. The hydrogen peroxide may be obtained by distillation under reduced pressure or by extraction with a suitable solvent.

Properties.—Pure hydrogen peroxide is unstable, sometimes decomposing with explosive violence. The dilute aqueous solution, however, is fairly stable, but the decomposition (into water and oxygen) is particularly susceptible to catalytic influence (colloidal or finely divided metals, especially silver and platinum, carbon, iodine, and alkalies). The solution, however, may be preserved by the addition of a little acid (phosphoric, tannic, and barbituric acids have been recommended). Hydrogen peroxide is an oxidising agent. It is employed for restoring pictures, the black lead sulphide, formed by the action of sulphuretted hydrogen on white lead, being oxidised to white lead sulphate. It liberates iodine from potassium iodide in the presence of ferrous sulphate—a very delicate test for hydrogen peroxide, and distinguishing it from other oxidising agents. When a solution of hydrogen peroxide is added to a colourless solution of titanium dioxide in sulphuric acid an orange or yellow colour is produced. One part of H_2O_2 in ten million can be thus detected. Hydrogen peroxide is widely used as a bleaching agent, and as the only products of its decomposition are water and oxygen, it is serviceable for bleaching materials that are destroyed by acids, alkalies, chlorine, etc. Ostrich feathers, bone, ivory, wood, silk, cotton, teeth, and hair are all bleached by hydrogen peroxide, aqueous solutions of which constitute "**auricome**," "**golden hair water**," etc. For bleaching wool, which is rendered a pure white and does not subsequently become yellow, the wool, after soaking in a dilute solution of sodium silicate, is placed in a peroxide bath containing sodium silicate. For very delicate materials 1 vol. of hydrogen peroxide (10 vols.) is diluted with 10 vols. of water. Some dentifrices consist of hydrogen peroxide mixed with gypsum and starch.

Hydrogen peroxide is a constituent of "**Sanitas**," and is extensively used in medicine as an antiseptic, being especially valuable in the treatment of alveolar abscesses and scrofulous and syphilitic sores.

The concentration of hydrogen peroxide solutions may be ascertained (1) by titration with standard potassium permanganate $\left(\frac{N}{10}=3.16\text{ g. }KMnO_4\text{ per litre}\right)$ in the presence of dilute sulphuric acid $\left(1\text{ c.c. }\frac{N}{10}\ KMnO_4=.0017\text{ g. }H_2O_2\right)$; (2) by treatment with excess of potassium iodide solution and subsequent titration of the liberated iodine with standard thiosulphate.

A 3 per cent. solution of hydrogen peroxide on decomposition yields approximately ten times its own volume of oxygen ("10 vol. peroxide").

II.—PERACIDS AND THEIR SALTS

LITERATURE

T. SLATER PRICE.—"Per-Acids and their Salts." 1912.

PERACIDS and the salts derived from them contain relatively more oxygen than the acids and salts bearing the same names without the prefix. The peracids, like the peroxides, may be divided into two classes:—(1) The *true* peracids, which may either be formed by the action of hydrogen peroxide on the lower acids or produce hydrogen peroxide as a product when decomposed with dilute sulphuric acid; and (2) the *pseudo* or false peracids (*e.g.*, perchloric acid) which are not related to hydrogen peroxide in this manner. The true peracids and their salts only are dealt with in this section.

Two persulphuric acids are known; permonosulphuric acid (Caro's acid), H_2SO_5, and perdisulphuric acid (usually called persulphuric acid), $H_2S_2O_8$.

Persulphuric Acid, $H_2S_2O_8$, is produced when sulphuric acid (D. 1.35-1.5) is electrolysed at low temperatures (5°-10°) with a high current density at the anode (Elbs and Schonherr, *Zeit. Elektrochem.*, **1**, 417 and 468; **2**, 245). The current density at the anode may be about 100 amperes per square decimetre. In the presence of sulphuric acid, persulphuric acid gradually undergoes hydrolysis to Caro's acid, which in turn is further hydrolysed to hydrogen peroxide and sulphuric acid.

$$(1)\ H_2S_2O_8 + H_2O = H_2SO_5 + H_2SO_4.$$

$$(2)\ H_2SO_5 + H_2O = H_2SO_4 + H_2O_2.$$

Anhydrous persulphuric acid is prepared by adding anhydrous hydrogen peroxide (1 mol.) to chlorosulphonic acid (2 mols.).

Properties.—The anhydrous acid is a crystalline solid melting at 65°. The aqueous solution has strong oxidising properties.

Permonosulphuric Acid (Caro's acid), H_2SO_5, may be prepared by treating potassium persulphate with concentrated sulphuric acid, or by the action of concentrated sulphuric acid on concentrated hydrogen peroxide (Baeyer and Villijer, *Ber.*, 1900, **33**, 124, 858, and 1569). The pure anhydrous acid is prepared by the gradual addition of the calculated amount of 100 per cent. hydrogen peroxide to well-cooled chlorosulphonic acid, $H_2O_2 + ClSO_3H = H_2SO_5 + HCl$.

Properties.—The anhydrous acid is a crystalline solid melting at 45°. The aqueous solution is fairly stable, and possesses an odour resembling that of bleaching powder. In the presence of sulphuric acid, Caro's acid undergoes hydrolysis to hydrogen peroxide. This reaction is used for the manufacture of hydrogen peroxide, *e.g.*, by distilling a mixture of potassium persulphate with sulphuric acid (D. 1.4) under diminished pressure (German Patents, 199,958, 217,538, 217,539; English Patents, 24,507 (1905), 23,660 (1910)).

The best known salts of persulphuric acid are the ammonium and potassium salts, which were first prepared by Marshall in 1891 (*Trans. Chem. Soc.*, 1891, **59**, 771; *Journ. Soc. Chem. Ind.*, 1897, **16**, 396).

Ammonium Persulphate, $(NH_4)_2S_2O_8$, is prepared by the electrolysis of a saturated solution of ammonium sulphate at a low temperature. To avoid cathodic reduction a diaphragm is used, saturated ammonium sulphate solution is placed in the anodic compartment, and sulphuric acid (1 : 1) in the cathodic compartment. The temperature of the anodic solution is maintained at about 15° by a stream of water running through coils. The anode consists of smooth platinum wire, the anodic current density being 500-1,900 amperes per square decimetre. Crystals of ammonium persulphate separate at the anode, and fresh ammonium sulphate must be supplied. The yield is increased by the presence of excess of sulphuric acid, and also by the addition of hydrofluoric acid. The current efficiency is about 70 per cent. (Elbs, *Journ. pr. Chem.*, 1893, **48,** 185; Müller and Schellhaas, *Zeit. Electrochem.*, 1907, **13,** 257). The electrolysis may be carried out without a diaphragm if the electrolyte is kept acid, and a high cathodic current density is employed (German Patents, 155,805, 170,311, 173,977).

Potassium Persulphate, $K_2S_2O_8$, may be prepared in a similar manner, or by the double decomposition of ammonium persulphate with potassium carbonate.

Properties.—Ammonium persulphate forms monoclinic crystals and potassium persulphate, either small prisms or tabular crystals. The latter salt is only sparingly soluble in water (1.76 in 100 at 0°). The dry persulphates are quite stable, but their aqueous solutions gradually decompose thus:—

$$K_2S_2O_8 + H_2O = 2KHSO_4 + O.$$

The persulphates are oxidising agents, liberating iodine from potassium iodide, oxidising ferrous salts to the ferric condition, etc. Silver salts exercise a marked catalytic effect on the oxidising properties of persulphates. Alkaline as well as acid solutions of persulphates have bleaching properties. Ammonium persulphate is used technically for introducing the hydroxyl group directly into the benzene nucleus, *e.g.*, *o*-nitrophenol is oxidised in alkaline solution to nitrohydroquinone. The ammonium salt is also used as a density reducer for negatives; the potassium salt, under the name "**anthion,**" is used as a hypo-eliminator in photography, but its use appears to be open to objections. Many of the alkaloids give colour reaction with persulphates, and some of them (*e.g.*, strychnine) are precipitated.

The estimation of persulphates is carried out by heating the solution with ferrous sulphate at 60°-80°, and titrating the excess of ferrous iron by means of standard potassium permanganate.

Perboric Acid has not been prepared in the free state, but **sodium perborate,** $NaBO_3 \cdot 4H_2O$, is a compound of considerable technical importance, and its preparation is the subject of many patents. When a 3 per cent. solution of hydrogen peroxide (120 parts) is added to a saturated solution of borax (20 parts) containing sodium hydroxide (4 parts), the resulting solution slowly deposits sodium perborate in a very pure but rather unstable form (Tanatar, *Zeit. physikal. Chem.*, 1898, **26,** 132; and 1899, **29,** 162). A coarsely crystalline and very stable product is obtained by dissolving borax (76.5 parts) and sodium hydroxide (21.6 parts) in 140 parts of boiling water, and pouring the resulting solution, cooled to about 60°, into a 3 per cent. solution of hydrogen peroxide (950 parts). After the solution has been well stirred, it is cooled to below 10° and allowed to crystallise slowly by standing undisturbed for some hours. The crystals are drained and washed with ice-cold water. A further crop may be obtained by stirring powdered salt into the mother liquor. The yield is 88 per cent. (Girsewald, German Patent, 1907, 204,279).

A sodium perborate called **perborax,** $Na_2B_4O_8 \cdot 10H_2O$, is prepared by gradually adding an intimate mixture of boric acid (248 g.) and sodium peroxide (78 g.) to well cooled water (2 l.). The separated crystalline product, after drying in air, contains 4.2 per cent. of active oxygen. It cannot be recrystallised from water, the first fraction which separates containing more active oxygen, and the later fraction less active oxygen than the original salt.

If hydrochloric acid, equivalent in amount to half the sodium in perborax, is added to an aqueous solution of the salt, ordinary sodium perborate separates.

Properties.—Sodium perborate contains a high proportion of active oxygen (10.4 per cent.). The aqueous solution is distinctly alkaline, and contains hydrogen peroxide. The salt is only sparingly soluble in water, but if it is added to dilute sulphuric acid, a highly concentrated solution of hydrogen peroxide is obtained. The aqueous solution exhibits oxidising properties, liberating iodine from potassium iodide, oxidising ferrous to ferric salts, etc. Sodium perborate is employed as a washing and bleaching agent. As a washing agent it possesses all the advantages of sodium peroxide, without many of the disadvantages of that compound. The older "dry" soaps consisted of soda, borax, and soap, but most of the modern washing powders contain sodium perborate or "**perborin**." "**Perborin M**" is a mixture of soap, soda, and sodium perborate; "**persil**" consists of soap, soda, sodium silicate, and sodium perborate; and "**clarax**" of sodium phosphate, borax, and sodium perborate.

Ammonium Perborate, $NH_4BO_3.\frac{1}{2}H_2O$, is obtained by adding ammonia to a solution of boric acid in aqueous hydrogen peroxide (2.5 per cent.). Barium, calcium, strontium, and copper perborates have been prepared, but they are unstable. The amount of active oxygen in a perborate is ascertained by titration with standard potassium permanganate in the presence of dilute sulphuric acid. Another method consists in treating 0.1 g. of the sample with an acidified solution of ferrous ammonium sulphate, the excess of which is subsequently titrated with titanous chloride (*Journ. Soc. Dyers*, 1910, **26**, 81).

Percarbonic Acid has not been prepared, but the potassium salt was prepared by Constam and Hansen in 1897.

Potassium Percarbonate, $K_2C_2O_6$, is prepared by the electrolysis of a saturated solution of potassium carbonate at −10° to 16°. When the current density is 30-60 amperes per square decimeter, aqueous potassium carbonate of density 1.56 on electrolysis at −10° gives a yield of percarbonate equal to 85-95 per cent. (*Zeit. Elektrochem.*, 1896-7, **3**, 137).

Properties.—Potassium percarbonate is a pale blue hygroscopic powder, which decomposes readily on warming:—

$$K_2C_2O_6 = K_2CO_3 + CO_2 + O.$$

It dissolves in ice-cold water with practically no decomposition. Potassium percarbonate is an oxidising agent, oxidising lead sulphide to lead sulphate, decolorises indigo, and bleaches cotton, wool, and silk. It is used as a bleaching agent and in photography under the name "**Antihypo**." By adding alcohol to a solution of sodium carbonate in 3 per cent. hydrogen peroxide, Tanatar obtained a product having a composition corresponding with the formula $Na_2CO_4.1\frac{1}{2}H_2O$. This product, however, in many respects differs from true per-salts, and consequently some chemists believe it to be sodium carbonate with hydrogen peroxide of crystallisation, $Na_2CO_3.H_2O_2.\frac{1}{2}H_2O$.

Sodium Percarbonate, $Na_2C_2O_6$, is prepared by adding sodium peroxide slowly to ice-cold absolute alcohol. Dry carbon dioxide is then passed into the mixture at 0°-5° for some hours. The crystalline mass is separated and washed with alcohol and ether.

The preparation of a sodium percarbonate, $Na_2CO_4.\frac{1}{2}H_2O$, from hydrated sodium peroxide and carbon dioxide, is described by Wolffenstein and Peltner (*Ber.*, 1908, **41**, 280; see also German Patents, 145,746 and 188,569).

This product is used as a disinfectant and for the preparation of hydrogen peroxide.

Percarbonates are estimated by treating a weighed quantity of the sample with dilute sulphuric acid, and titrating the hydrogen peroxide formed with standard potassium permanganate.

Salts of several other peracids have been prepared, but at present have no technical importance.

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